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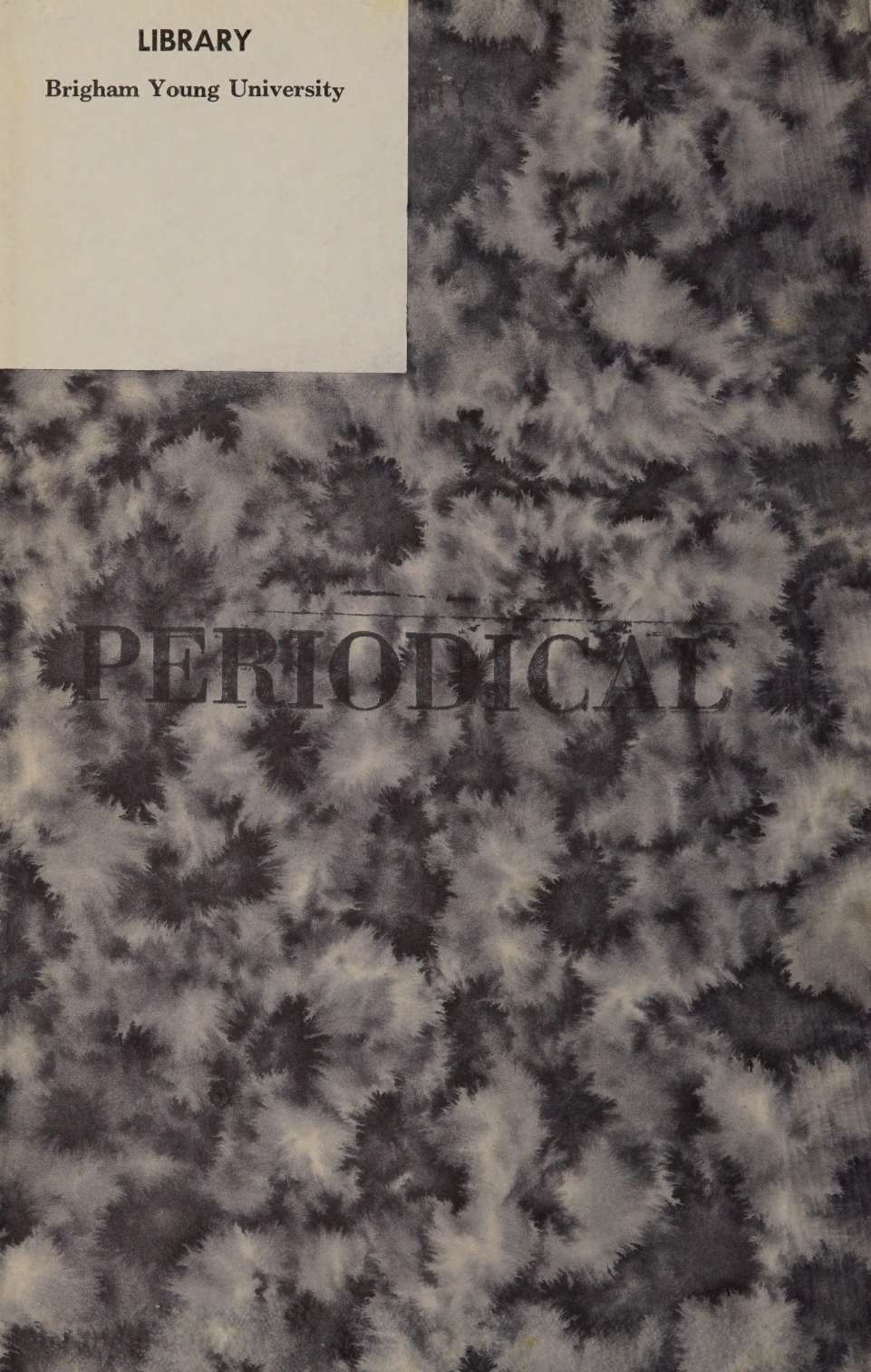

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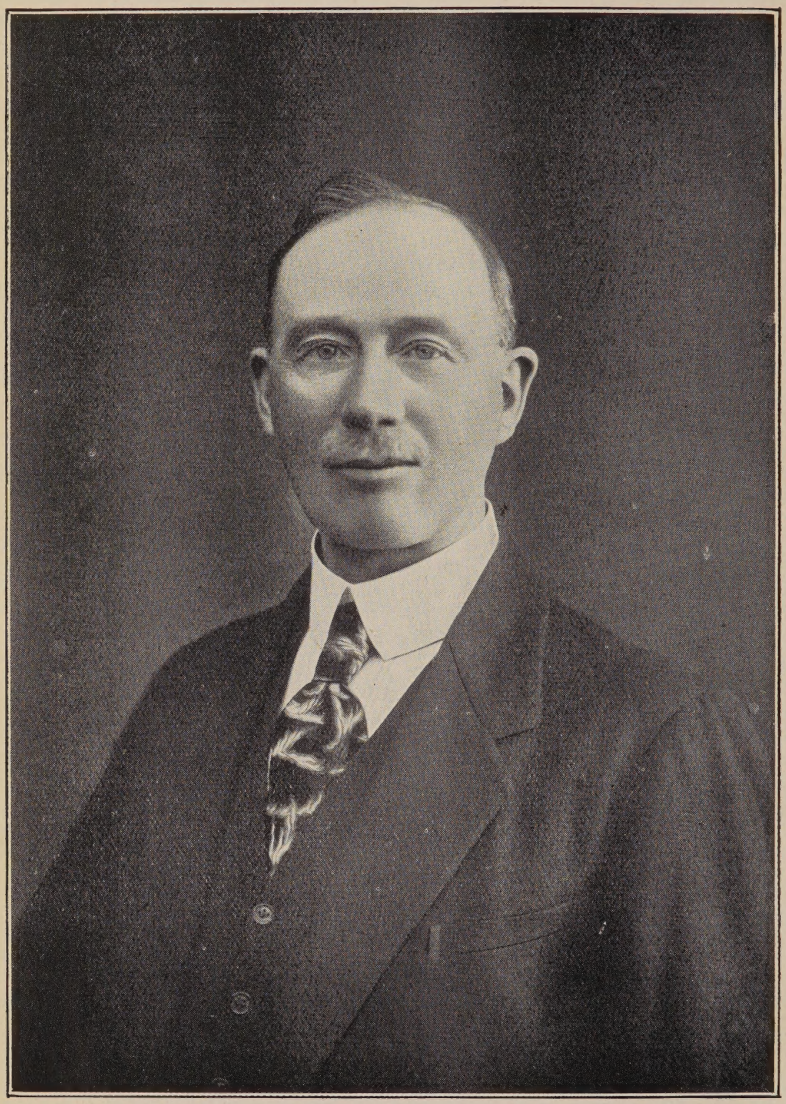

A. G. RICHARDSON, Esq.,

President for Session, 1924-25.

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TRANSACTIONS

OF

THE CERAMIC SOCIETY

INCLUDING

THE REFRACTORY MATERIALS SECTION.

Founded in 1900 as "The North Staffordshire Ceramic Society," and continued from 1903 to 1916 as "The English Ceramic Society."

VOLUME XXIV.—SESSION 1924-25.

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PUBLISHED BY THE SOCIETY:
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RULES.

(Subject to modification by recommendations from the Refractory Materials Section).

1.—The Society shall be called THE CERAMIC SOCIETY. It shall comprise a special section dealing with Refractory Materials.

2.—The object of the Society shall be the discussion of all subjects relating to the industries connected with Clay Working and Refractory Materials.

3.—Persons desirous of membership shall be proposed and seconded by two Members of the General Meeting, and they are then eligible for election at the next Council Meeting.

4.—The Society shall be governed by a President, Past-Presidents, Vice-Presidents, a Council, a Librarian, a Secretary, and a Treasurer. The President shall be elected in alternate years by the Pottery Section and by the Refractory Materials Section, and shall, upon the expiration of his year of office, become Chairman of his own Section for the ensuing year. The Office of Past-President shall be held by retiring Presidents. The Pottery Section, and the Refractory Materials Section, shall each elect three Vice-Presidents, one of whom shall retire annually, and shall not be eligible for re-election until after the lapse of one year. Other Officers shall be elected at the last General Meeting of each Session, and shall hold office until the last General Meeting of the ensuing Session, when they shall be eligible for re-election. A Chairman of Council shall be appointed by the Council.

4a.—The Council shall consist of officers, Past-Presidents, Vice-Presidents and twelve members, of whom four shall resign each year, the retiring members to be eligible for re-election.

4b.—Two additional members of the Council, one of whom will also act on the Publication Committee, shall be elected by the Federation of Pottery Manufacturers.

5.—The headquarters of the Society shall be the Central School of Science and Technology, Stoke-on-Trent.

6.—The Meetings shall be fixed from time to time as arranged by the Sectional Committees. At Stoke-on-Trent the Meetings during the Session are usually held at 7-30 p.m. on the second Monday of the month.

7.—The annual subscription shall be payable in advance, and shall be fixed from time to time by the Committee (25/- for 1925-26). Members of the Society who have paid their annual subscription receive a copy of the TRANSACTIONS free.

8.—A firm can join the Society by paying an annual subscription of two guineas. For this subscription the attendance at each meeting shall be limited to three members of the firm, and one copy of the TRANSACTIONS will be supplied free annually.

9.—New members shall pay an entrance fee of one guinea.

10.—Students may be elected to Student Memberships without paying an entrance fee. Their subscription shall be 5/-, and will entitle them to attend the meetings, but no TRANSACTIONS will be supplied. After twelve months membership, a Student can be elected to full membership without payment of entrance fee. The Council shall decide whether a person is eligible for a Student Membership.

11.—Notification of meetings shall be sent by post to each member in Great Britain with the name of the subject of the paper for discussion.

12.—In the discussions arising upon any paper, no speaker shall occupy more than ten minutes, or make more than one speech, except by the permission of the Chairman.

RULES—*Continued.*

13.—Any property of the Society lent to members must be returned within a week.

14.—Any member promising a paper and failing to keep his appointment shall himself provide a substitute.

15.—The Society shall have the prior right of publication of all papers read before it for a period of three months.

16.—Authors must send their papers to the Society before or immediately after the communication has been read. If received in time the paper may be printed in time for the meeting. The official receipt of any paper will be dated from the time it is received by the Secretary.

17.—Members may obtain one copy of each of the back numbers of the TRANSACTIONS at subscription rates, providing they are for their own personal use, and that the number in stock be over 18.

18.—Members who are three years in arrear with their subscriptions shall be informed by means of a printed notice, and if the arrears are not paid within a month their names shall be struck off the list. *New Members are put on the list of members when their subscriptions have been paid.*

19.—A member of the Society may introduce a visitor to an ordinary meeting. A visitors' book is kept to show what non-members are present, and by whom they are introduced. The names of the visitors are read out by the Chairman at the opening of the same meeting.

20.—No alteration or addition to the above Rules shall be made except notice be given in General Meeting, and passed by the ensuing General Meeting. Ten to form a quorum.

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COLMAN, H. G., D.Sc., Ph.D., 1, Arundel Street, Strand, W.C. (1916-17)
COLVILLE, DAVID, & SONS, Ltd., 195, West George Street, Glasgow .. .. (1917-18)
CONSETT IRON Co., Ltd., Consett, Durham .. .. (1920-21)
CONSTRUCTION DE FOURS: CIE GE de 32 et 34, Rue de la Grange-aux-Belles, Paris. XC. .. .. (1918-19)
COOKE, A. W., 40, High Street, Wolstanton .. .. .. (1918-19)
COOPER, H. F., 38, Trent Terrace, Hanley .. .. .. (1921-22)
COPPEE, Co., Ltd., 44, Grosvenor Place, London, S.W., 1 .. (1918-19)
CORN, E. R., Henry Richards Tile Co., Tunstall .. .. (1908-09)
CORN, E. R. G., Tolima, Trentham .. .. (1918-19)
COTTON, A., Nelson Pottery, Hanley .. .. (1912-13)
COTTON BROS., Portland Road, Longton, Stoke-on-Trent .. (1918-19)
COUPAR, A., Bassilow Farm, Fenton, Stoke-on-Trent .. (1914-15)
COX, PAUL E., Dept. of Ceramic Engineering, Iowa State College, Ames, Iowa, U.S.A. .. .. (1912-22)
CRAWFORD, GEORGE, c/o Messrs. Stone & Co., Ltd., Nonsuch Firebrick Works, Epsom, Surrey. (1924-25)
CRONQUIST, G. W., Hëlsingborg, Sweden .. .. .. (1922-23)
CRONSHAW, Dr. H. B., Technical Institute, Brierley Hill, South Staffs. .. .. (1920-21)
*CROW, ROBERT, c/o Australian Porcelain Co., Ltd., 434, Law Courts Place, Melbourne, Australia .. .. (1918-19)
CULLINAN, D., Olifants Fontein, Transvaal, S. Africa .. (1921-22)
CULLINAN, R. V., c/o Box 286, Johannesburg, S. Africa .. (1913-14)
CUMING, N. F., c/o Cuming, Smith & Co., Ltd., 65, William Street, Melbourne, Australia .. .. (1921-22)
CYPLES, W. H., Trentham Road, Longton .. .. .. (1906-07)

*DALE, A. J., 11, Colclough Road, Meir, Stoke-on-Trent .. (1922-23)
DAVIDSON, J. H., M.Sc., Messrs. Wood Bros., Glass Co., Ltd., Pontefract Road, Barnsley. .. .. (1903-04)
DAVIE, C., Messrs. N. B. Allen & Co., Ltd., Hirwain, South Wales .. .. (1917-18)
DAVIS, TURNBULL & Co., 4 & 5, Prudential Buildings, Sheffield .. .. (1920-21)
DAVIS, F. W., 342, Uttoxeter Road, Longton .. .. .. (1923-24)

DAVISON, J. A., Porthill, Stoke-on-Trent .. .. .. (1905-06)
DEB, S., 45, Tangra Road, Calcutta, India .. .. .. (1918-19)
DENNIS, F. W., Holly Cottage, Ricardo Street, Dresden .. (1911-12)
DERBYSHIRE SILICA FIRE BRICK Co., Friden Station, Hartington, near Buxton .. .. (1921-21)
DERRY, B. R., Hazlehurst, Blurton Road, Fenton.. .. .. (1923-24)
DETROIT PUBLIC LIBRARY, Detroit, Mich, U.S.A. .. (1922-23)
*DEVEREUX, P. S., c/o The British Abrasive Wheel Co., Ltd., Tinsley, Sheffield .. .. (1912-13)
DUNSMUIR, G., c/o Hillview, Bonnybridge, Stirlingshire .. (1916-17)
DODD, W. H., 147, Bucknall New Road, Hanley, Stoke-on-Trent (1909-10)
DOLBY, W. J., 24, Whitfield Avenue, Newcastle, Staffs. .. (1920-21)
DOUGALL, JAMES & SONS, Ltd., Firebrick Works, Bonnybridge, Stirlingshire .. .. (1916-17)
DOUGLAS FIREBRICK Co., Ltd., Kilwinning .. .. (1916-17)
DRESSLER TUNNEL OVENS, Ltd., Holmthorpe, Redhill, Surrey .. .. (1916-17)
DRESSLER, PHILIP, 1543, East Boulevard, Cleveland, Ohio, U.S.A. .. .. (1918-19)
*DUFFIELD, F., L, The Derbyshire Basic Co., Ltd·, 99 Pinstone Street, Sheffield .. .. (1921-22)
DUNN, F. T., Messrs. The Henry Richards Tile Co., Tunstall, Stoke-on-Trent .. .. (1906-07)
*DUNN, J. T., D.Sc., F.I.C., Public Analysts' Laboratory, 10, Dean Street, Newcastle-on-Tyne .. .. .. (1916-17)
DYSON, J. & J., Ltd., Griffs Fireclay Works, Stannington, nr. Sheffield .. .. (1922-23)

EARDLEY, DONALD, 21, Cobden Street, Dresden, Stoke-on-Trent .. .. (1920-21)
EDWARDS, A. O., c/o The Yorkshire Refractories Co., Ltd., 27, Waterdale, Doncaster .. .. (1917-18)
EDWARDS, J. C., Terra Cotta Works, Ruabon .. .. (1921-22)
EDWARDS, W. H., Park Lane, Fenton, Stoke-on-Trent .. (1921-22)
EDWARDS, C., Rosslea, 4, Aspley Road, Wandsworth, London, S.W.18 .. .. (1914-15)
EGLINTON MAGNESITE BRICK Co., Ltd., Dundyvan Brick Works, Coatbridge .. .. (1917-18)
ELLAND FIRECLAY Co., Ltd., Calder Fireclay Works, Elland (1916-17)
ELLIS, THOS., Penwyllt, near Neath .. .. (1916-17)
ELEY, ERNEST E., 15, Lord Street, Basford, Stoke-on-Trent (1920-21)
*EMERY, W., 7, Catherine Street, May Bank, Staffs. .. .. (1902-03)
EMERY, W. L., Kensington Pottery Ltd., Statham St., Hanley (1924-25)
ENDELL, K. Dr., Berlin Steglitz, Breitestrasse 3, Germany.. (1920-21)
ETCHELLS, H., 56, Westwood Road, Sheffield.. .. .. (1917-18)
EVERITT, CHARLES KINGSTON, c/o Edgar Allen & Co., Ltd., Imperial Steel Works, Sheffield .. .. .. (1916-17)

FAILL, JAMES, 146, West Regent Street, Glasgow .. .. (1916-17)
FARNLEY IRON Co., Ltd., Farnley, near Leeds .. .. (1916-17)
FEARNSIDES, W. G., 11, Ranmoor Crescent, Sheffield .. (1916-17)
FERGUSON, R. F., Box 74, Bolivar, Pa., U.S.A... .. .. (1923-24)
FERN, E. R., School of Art, Bombay .. .. (1906-07)
FIDLER, F., Spring Bank, Wigad .. .. (1925-26)
*FIELDING, A., Devon Pottery, Stoke-on-Trent .. .. (1902-03)
FIELDING, R., Devon Pottery, Stoke-on-Trent .. .. (1906-07)
FINN, R., 2, Eaton Street, Hanley .. .. (1920-21)
FOLEY, F. D., Loch Lomond Road, St. John's, N.B., Canada (1917-18)
FORD, SAMUEL & Co., Lincoln Pottery, Burslem .. .. (1921-22)
FOSTER, HENRY & Co. Ltd,, Backworth, Newcastle-on-Tyne (1916-17)
*FOSTER, J. E., 48, Gilman Street, Hanley .. .. .. (1909-10)
*FOX, W. G., 44, Riseley Road, Hartshill, Stoke-on-Trent .. (1912-13)

FREEMAN, Dr. LUDFORD, Abbotsthorpe, Carnarvon Road, Redland, Bristol .. .. (1914-15)
FULPER, W. H., c/o The Fulper Pottery Co., Flemington, N.J., U.S.A. .. .. (1910-11)

GARDNER, W. J., c/o The Meltham Silica Brick Co., Ltd., Meltham, near Huddersfield.. .. .. (1916-17)
GARDNER, W. T., F.C.S., 14, Beechwood Avenue, Kew Gardens, London, S.W. .. .. (1918-19)
GATENSBURY, H. R., Atlas Foundry, Victoria Road, Hanley (1913-14)
GELSTHARP, F., Director of Research, Pittsburgh Plate Glass Co., Creighton, Pa. .. .. (1911-12)
GIBBONS, Ltd., Dibdale Works, Dudley .. .. .. (1916-17)
GIBBS, A. E., 1012, Widoner Buildings, Philadelphia, Pa., U.S.A. .. .. (1918-19)
GIBSON, W. F., ... (1923-24)
GILL, W. R., Cleveland Villa, Castleford, Yorkshire.. .. (1909-10)
GILL, G. M., 119, Victoria Street, London, S.W.1... .. .. (1922-23)
GIMSON, J. F., 69, Fountain Square, Fenton, Stoke-on-Trent (1920-21)
GINORI, RICHARD, Soc. Ceramica, Colonnata, Florence, Italy (1924-25)
GINOU, RICHARD, Milano, Casella Postale n 1261 Societa Ceramica .. .. (1924-25)
GEPP, H. W., General Manger, Electrolytic Zinc Co. of Australasia, Box, A.A., Hobart, Tasmania .. .. .. (1918-19)
GLENBOIG UNION FIRECLAY Co., Ltd., Glenboig, Scotland (1916-17)
GLEAVES, E., Alsager House, Marsh Avenue, Wolstanton, Stoke-on-Trent .. .. (1920-21)
GLOVER, SAMUEL, F.R.M.S., Olive Mount, St. Anns, St. Helens .. .. (1916-17)
GODDARD, J. V., Trentham .. .. (1905-06)
GODDARD, A. H., c/o Messrs. G. L. Ashworth Bros., Ltd., Hanley .. .. (1918-19)
GOODWIN, F. T. H., Hollydean, Park Avenue, Longton .. (1910-11)
GOODWIN, W. E., Watcombe House, 225, Waterloo Road, Burslem .. .. (1902-03)
GOODWIN, JOHN, Foley Works, Fenton, Stoke-on-Trent .. (1920-21)
GOSLING, JAS., Atlas Foundry, Victoria Road, Hanley .. (1913-14)
GOSS, W. H., Falcon Pottery, Stoke .. .. (1914-15)
GRAHAM, J. W., Ashley Villa, Lancaster Av., Newcastle Staffs. .. .. (1914-15)
GRAY, A. E., Glebe Works, Mayer Street, Hanley .. .. (1917-18)
GRAY, J., Auldhaven, Milngavie .. .. (1918-19)
GRAYSON, LOWOOD, J. & Co., Ltd., Deepcar, near Sheffield (1916-17)
GREAVES-WALKER, A. F., Box 1122, Pittsburgh, Pa, U.S.A. .. .. (1920-21)
*GREEN, A. T., 138, Dimsdale Parade, Wolstanton, Staffs. .. (1917-18)
GREEN, G. D., Hobbergate, Brampton, Newcastle .. .. (1921-22)
GREEN, J. C., 49, Bromley Road, Kingswinsford, Staffs. .. (1911-12)
GREEN, R. A., 3, Brocksford Street, Fenton .. .. .. (1924-25)
*GREEN, S. A., Brampton Hill, Newcastle, Staffs. .. .. (1905-06)
GREGORY, C., Newfield, Willington, Co. Durham .. .. (1916-17)
GREGORY, J. G. & SON, Friars Street, Newcastle, Staffs .. (1921-22)
GREGORY, REDDISH & Co., Ltd., Silica & Firebrick Works, Deepcar, near Sheffield .. .. (1916-17)
GRICE, E., 21, Station Road, Meir, Longton, Staffs.. .. (1913-14)
GRIMWADE, C. D., Fairlands, Trent Vale, Stoke-on-Trent .. (1918-19)
GRINDLEY, W. H., Woodland Pottery, Tunstall .. .. (1906-07)
GROCOTT, W., 75, Shenstone Road, Edgbaston, Birmingham (1918-19)

HAGUE, A. P., c/o Cammell Laird & Co., Ltd., Cyclops Steel and Iron Works, Sheffield .. .. (1920-21)
HALL, Hy., The Bungalow, Botteslow, Hanley.. .. .. (1912-13)

HALL, J. & Co., Stourbridge .. .. (1916-17)
HALLIDAY, H., 25, Victoria Street, Westminster, London, S.W. (1923-24)
HAMILTON, J., Ideal Pottery, Trenton Potteries Co., Trenton, U.S.A. .. .. (1906-07)
HAMILTON, WILLIAM, 41, St. Vincent Place, Glasgow, C1. .. (1917-18)
HAMMOND, PERCY, Newbridge House, Bollington, Macclesfield .. .. (1916-17)
HAMMOND, WILLIAM, Jevington, Bollington, Macclesfield (1916-17)
HAMPTON, T. E., Eastwood Marl Works, Hanley .. .. (1908-09)
HANCOCK, E. A., Kepax, Worcester .. .. (1916-17)
*HANCOCK, W. C., B.A., F.I.C., 60, Greek Street, Soho Square, London, W.1 .. .. (1917-18)
HARBORD, F. W., 16, Victoria Street, London, S.W. .. (1916-17)
HARDING, F. W., 6, Hassell Street, Hanley .. .. .. (1921-22)
HARRIS, GUY, Messrs. Bullers, Ltd., Milton .. .. .. (1922-23)
HARRISON, A. C. Bath Street, Hanley .. .. .. (1910-11)
HARRIMAN, WM., & Co., Ltd., 51, Westgate Road, Newcastle-on-Tyne .. .. (1917-18)
HARRINGTON, T. H., The Harrington Tile Co., Walker Street, Tunstall .. .. (1913-14)
HARRINGTON, A., Lower Hill Farm, Mow Cop, Stoke-on-Trent (1923-24)
HARRISON, T. S., May Place, Newcastle, Staffs. .. .. (1921-22)
HARRISON, J. H., Godolphin House, Wolstanton, Stoke-on-Trent .. .. (1923-24)
HARTLEY, H. L., Castleford Pottery, Castleford, Yorks .. (1917-18)
HARTMANN, M. L., The Carborundum Co. Niagara Falls, N.Y., U.S.A. .. .. (1921-22)
HARVEY, G., 78, Baskerville Road, Hanley .. .. .. (1921-22)
HASSALL, W., Tresco House, Woodville, Burton-on-Trent (1920-21)
HAUNCHWOOD BRICK & TILE Co., Ltd., Nuneaton .. (1921-22)
HAWLEY, ERNEST, c/o Messrs. Hawley & Jackson, Longton (1913-14)
HAWLEY, W. S., Fairmont, Sunny Bank Road, Newcastle, Staffs. .. .. (1908-09)
*HEATH, A., 71, Park Road, Hanley .. .. (1900-01)
HEATH, B. C., St. Edmunds Avenue, Porthill, Staffs. .. .. (1921-22)
HEATH, C. H., High Street, Woodville, near Burton-on-Trent (1915-16)
HEATH, F., 35, Harpfield Road, Trent Vale, Stoke-on-Trent .. (1923-24)
HEATON, WM., Ravenhead Brick Co., Upholland, near Wigan (1917-18)
HENDERSON, H. B., 1538, N. High St., Columbus, Ohio, U.S.A. .. .. (1911-12)
HENDERSON, J. D., c/o The Anglo-Greek Magnesite Co., 24, Finsbury Square, London, E.C. .. .. (1917-18)
HEPWORTH IRON Co., Ltd., Hazlehead, near Sheffield .. (1916-17)
HEYS, F. R., Hydro., Kilmacolm, Scotland .. .. .. (1921-22)
HEWITT, A. E., Easedale, Trentham, Stoke-on-Trent .. (1912-13)
HEWITT, F. G., 6, Boughey Street, Stoke-on-Trent .. .. (1918-19)
HIGGINS, F. W., Carborundum Co., Ltd., Trafford Park, Manchester .. .. (1918-19)
HILL, WESTLAKE & Co., Ltd., 8 Gloucester Sq., Southampton (1920-21)
HIMLEY FIRE & RED BRICK Co., Ltd., near Dudley .. (1916-17)
HINCHLIFFE, HERBERT, Bullhouse Colliery, Penistone, Sheffield .. .. (1917-18)
*HIND, S. R., 48, Colclough Road, Meir, Stoke-on-Trent .. (1918-19)
HITCHEN, W., 12, Denby Lane, Heaton Chapel, Stockport .. (1923-24)
HOBBS, W. L., Dyserth, Flintshire .. .. (1916-17)
HODSON, G. A., c/o The Hathern Station Brick & Terra-Cotta Co., Ltd., Loughborough .. .. (1908-09)
HOLCROFT, N. P., Holmlea, Market Street, Milton, Stoke-on-Trent .. .. (1923-24)
*HOLDCROFT, A. D., Bradwell Lane, Wolstanton .. .. (1902-03)

*HOLDCROFT, J. P., Bradwell Lane, Wolstanton .. .. (1902-03)
HOLDCROFT, L., Stockton Brook, Stoke-on-Trent .. .. (1923-24)
HOLLINGWORTH, D. V., F.I.C., F.C.S., Beechwood, Kidsgrove, near Stoke-on-Trent .. .. (1924-25)
HOLLINSHEAD, THOMAS, 42, Princes Road, Hartshill, Stoke-on-Trent .. .. (1924-25)
HOPE, H., Devonmoor Art Pottery Co., Ilsington, nr. Newton Abbot .. .. (1907-09)
HOPE, G. F. W., The Dingle, Fingringhoe, Colchester .. .. (1920-21)
*HOULDSWORTH, H. S., 10, Rydal Terrace, Heckmondwicke, Yorks .. .. (1921-22)
HOWELL, W. E., 41, Sneyd Terrace, Burslem .. .. .. (1915-16)
HOWLETT, H. & Sons, Boundary Street, Hanley .. .. (1918-19)
HOWIE, F. C., Hurlford Fireclay Works, Kilmarnock .. (1916-17)
HOWSON, R. G., c/o Messrs. G. Howson & Sons, Limited, Hanley .. .. (1907-08)
HUBBARD, A. E., 64, Psalter Lane, Sharrow, Sheffield .. .. (1922-23)
HUGHES, F. S., Opal China Works, Fenton, Staffs. .. .. (1909-10)
HUGILL, W., B. Met. 5, Falmouth Road, Abbeydale, Sheffield (1923-24)
HULL, R., Junr., Wellcroft, Caverswall Lane, Blythe Bridge (1923-24)
HULSE, H. J., Drubbery Lane, Longton, Stoke-on-Trent .. (1924-25)
HUNT, PERCY, Whiteley Cottage, Marehay, Derbyshire .. (1921-22)
HURLL, Ltd., P. & M., 144, West Regent Street, Glasgow .. (1917-18)
HUTTON, R. S., D.Sc., Castle Hill, High Wycombe, Bucks .. (1916-17)

IVERS, B., Marikuppam, Kola Gold Fields, South India .. (1922-23)

JACKSON, CHARLES E., Warwick China Co., Wheeling, Pa., U.S.A. .. .. (1922-23)
JACKSON, E. W., F.I.C., Godrevy, Saltburn-by-the-Sea .. (1918-19)
JACOBSEN, CARL, Malmegade 7, Copenhagen, Denmark
JEFFERY, Dr. J. A., c/o Champion Porcelain Co., Detroit, Mich., U.S.A. .. .. (1917-18
JEPPSON, G. N., 41, Burncoat Street, Worcester, Mass., U.S.A. .. .. (1912-13)
JOHNSON, A., 11, Hillside Cottages, Glenboig, near Glasgow (1922-23)
JOHNSON, A. S., c/o Messrs. Alfred Meakin, Ltd., Tunstall.. (1909-10)
JOHNSON, S. Ltd., Brittania Pottery, Burslem, Stoke-on-Trent .. .. (1920-21)
JOHNSTON, T. B., Canynage Road, Clifton, near Bristol .. (1918-19)
JOHNSON, E., c/o Messrs. W Boulton, Ltd., Navigation Rd., Burslem .. .. (1909-10)
JOHNSON, H., Tile Manufacturer, Highgate Tile Works, Tunstall .. .. (1906-07)
JOHNSON, J., Talke and Alsager Road, Alsager .. .. (1912-13)
JOHNSON, R. L., Oulton Rocks, Stone, Staffs... .. .. (1912-13)
JOHNSON, W. P., B.Sc., Foundry Lane, Wallheath, near Dudley .. .. (1910-11)
JOHNSON, H. C., Clayton Hall, Newcastle, Staffs. .. .. (1923-24)
JONES, A. B., Junr., Grafton Works, Longton .. .. .. (1914-15)
JONES, A. E. & Co., Ltd., Palissy Pottery, Longton .. (1924-25)
JONES, A. G., Lynton, Trentham, Staffs. .. .. .. (1909-10)
JONES, A. G. H., Heath House, Uttoxeter .. .. .. (1905-06)
JONES, CHARLES, Heatherfield, Bwlchgwyn, near Wrexham (1916-17)
JONES, CHESTER H., 1570, Old Colony Buildings, Chicago, U.S.A. .. .. (1921-22)
JONES, GEO., & SONS, Ltd., Crescent Pottery, Stoke-on-Trent (1921-22)
JONES, L. Southwood, c/o Messrs. Southwood, Jones & Co., Danycraig Works, Risca, Monmouth .. .. .. (1916-17)
JONES, N. L., c/o J. & G. Meakin, Ltd., Hanley .. .. (1914-15)

*JONES, R. H. H., Riversdale, Keyberry Road, Newton Abbot (1900-01)
JONES, Sir W. J. 17, Victoria Street, Westminster, S.W.,1 .. (1916-17)
JONES, W. R., "Wagon and Horses" Hotel, Wallheath, nr. Dudley (1921-22)
JONES, W. R. D., University College, Cardiff .. .. .. (1921-22)
JONES, AUSTIN, c/o Messrs. Edwards & Jones, Engineers, Longton, Stoke-on-Trent .. .. (1922-23)

KANHÄUSER, Dr. FRANZ, Chodovu Karl, Karlwych, Varo, Czechoslovakia .. .. (1922-23)
KEELING, F. A., c/o Messrs. Keeling & Walker, Stoke-on-Trent .. .. (1906-07)
KEELING, J., c/o Keeling & Co., Dalehall, Burslem .. .. (1906-07)
KEELING, G. A., Brown Edge Road, Stockton Brook, Stoke-on-Trent .. .. (1918-19)
KENT, W. F., 72, Leonard Street, Burslem .. .. .. (1903-04)
KENT, W. J., c/o. Messrs. Taylor Tunnicliff & Co., Hanley, Stoke-on-Trent .. .. (1920-21)
KIRKLAND, H. S., Albion Pottery, Etruria, Stoke-on-Trent (1906-07)
KLEIN, CARL, A., 4, Brimsdown Av., Enfield Highway, Middlesex .. .. (1915-16)
KNIGHT, W. C., Westholme, Barnfields, Penkhull, Stoke-on-Trent.. .. .. (1908-09)
KOPPERS, Dr. H., Malthestrasse 29, Essen .. .. .. (1923-24)
KREHBIEL, J. F., 168E, Lake View Avenue, Columbus, Ohio, U.S.A. .. .. (1917-18)

LACLEDE CHRISTY CLAY PRODUCTS Co., 1673, Royal Exchange Building, St. Louis, Missouri, U.S.A. .. .. (1924-25)
LANCASTER, E., Lyndhurst, Trentham .. .. .. (1914-15)
LEACH, C. A., Padeswood, Weston Coyney, Stoke-on-Trent.. (1922-23)
LEATHER, J. P., Pendle, 6, Sollershott East, Letchworth, Herts. (1916-17)
LEEDS FIRECLAY Co., Ltd., Wortley, Leeds.. .. .. (1916-17)
*LEESE, A., 81, Vivian Road, Fenton, Staffs. .. .. .. (1900-01)
LESSING, R., PhD., The Laboratory, Southampton House, 317 High Holborn, London .. .. (1910-11)
LEWIS, E. H., The Green, Wishaw, Scotland .. .. .. (1917-18)
LILLESHALL (The) Co., Ltd., Priors Lee Hall, Shifnal, Salop (1916-17)
LILLIBRIDGE, H. D., c/o American Encaustic Tiling Co., Ltd. Zanesville, Ohio, U.S.A. .. .. (1916-17)
LINDOP, R. C., 41, Grove Road, Fenton.. .. .. .. (1913-14)
LINSTRUM, T., Peacocks Bdg., 23, Park Row, Leeds.. .. (1917-18)
LINTON, ROBERT, 1151 So. Broadway, Los Angeles, California .. .. (1925-26)
LLOYD, HORACE, Messrs. N. B. Allen & Co., Ltd., Hirwain, South Wales .. .. (1917-18)
LLOYD, W. J., Rothesay, King's Avenue, Wolstanton .. (1915-16)
LLOYD, T. H., c/o The Pure Bone Phosphate Co., 27, Kirkgate, Newark .. .. (1918-19)
LOCKHART, D. B., Victoria Pottery, Pollokshaws, Glasgow (1918-19)
LOUDON, JOHN, Loudon & Russell, Ltd., Allanton Fireclay Works, Newmains, Scotland.. .. .. (1917-18)
LOVATT, L. D., 79, Festing Street, Hanley .. .. .. (1916-17)
LOXTON, N. G., Leeds Fireclay Co., Burmantofts Works, Leeds (1918-19)
LUCAS, W. T., The Limes, Alsager .. .. (1921-22)
LYSAGHT, J., Ltd., Normanby Park Works, Scunthorpe, Lincs. (1918-19)

MACHIN, C. W., 65, Trentham Road, Longton .. .. (1914-15)
McGAVIN, WILLIAM, c/o The Priestman Collieries, Ltd., Whinfield, Rowlands Gill, nr. Newcastle-on-Tyne.. .. (1923-24)
Mc KINLAY, PARKER, "Benhar," Otago, New Zealand .. (1921-22)
MACLEOD, W. A., 17, Gayton Road, Harrow-on-the-Hill .. (1923-24)

McNEAL, C., Lloyds Bank Chambers, Fenton, Staffs. .. .. (1910-11)
MacWHIRTER, J., Elsinore, Milngavie, Scotland .. .. (1917-18)
McCORMICK, J., Dock Office, Hull, Yorks. .. .. .. (1917-18)
McCANCE, Dr. A., Westview, Uddingston .. .. .. (1918-19)
McDOWELL, J. S., 1800, Farmers Bank Buildings, Pittsburgh, U.S.A. .. .. (1918-19)
MALKIN, S., c/o The Malkin Tile Works Co., Burslem .. (1905-06)
MALKIN, W. F., Dalehall Mill, Burslem .. .. .. (1914-15)
MALKIN, J. R., Penryn, Grosvenor Place, Wolstanton .. (1918-19)
MANSFIELD, F., 9, Red Cross Street, Liverpool .. .. (1918-19)
MARLOW, J. H., 19, The Villas, Stoke-on-Trent .. .. (1916-17)
MARSHALL, F. J., 48, Mayer Street, Hanley .. .. .. (1911-12)
MARSHALL, W., Fern Dale, Bushbury Road, Heath Town, Wolverhampton .. .. (1924-25)
*MARTIN, GEOFFREY Dr., Woodleigh, Bassingham Road, Wembley, N. .. .. (1921-22)
MASON, ADAM & SONS, Ltd., Horwich, Lancashire.. .. (1916-17)
MASSACHUSETTS INSTITUTION OF TECHNOLOGY, Massachusetts Avenue, Cambridge Mass., U.S.A. .. .. (1922-23)
*MAYER, E. W. T., 11, Westwood Road, Wolstanton.. .. (1914-15)
MEAKIN, J. & G., Ltd., Eagle Pottery, Hanley, Stoke-on-Trent (1918-19)
MEIR, J., The Barn, Grosvenor Place, Wolstanton .. .. (1911-12)
MELLOR, BERT, 16, Pottery Road, Bovey Tracey, Devon .. (1924-25)
*MELLOR, J. W., D.Sc., Sandon House, Regent St., Stoke-on-Trent .. .. (1904-05)
MELLOR, G. & Co., Ltd., Etruria Vale Mills, Stoke-on-Trent .. (1923-24)
MEREDITH, J., New Villas, Shirley Road, Hanley .. .. (1911-12)
MICHELSEN, H. C., 33, Vestergade, Copenhagen .. .. (1921-22)
MICHIE, A. C.,12, Akenside Hill, Newcastle-on-Tyne .. (1910-11)
MIDDLETON FIRECLAY WORKS, Leeds .. .. .. (1916-17)
MITCHELL, JOHN, c/o A. Y. Dinas Silica Brick Co., Ltd., 142, Queen Street, Glasgow .. .. (1916-17)
MITCHELL, J. S., Hyland, Hargate Drive, Hale, Manchester (1917-18)
MOKIJI, ICBIJE, c/o. Kurasaki Togio Co., Kurasaki machi, Fukuokaken, Japan. .. .. (1922-23)
MOLLER, C. A., Vestergade, 33, Copenhagen, Denmark .. (1921-22)
MOMOKI, S., c/o Toyo Tokio Kwaisha Ltd., Shinozaki, nr. Kokura City, Japan .. .. (1916-17)
MONTGOMERY, ROBERT J., The Mining Building, University of Toronto, Toronto 5, Ont. .. .. (1918-19)
MONTGOMERY, ALLAN W., 58, York Street, Glasgow .. (1918-19)
*MOORE, B., Wolfe Street, Stoke-on-Trent .. .. .. (1900-01)
*MOORE, BERNARD, J., The Gables, Bromley Hough, Penkhull, Stoke-on-Trent .. .. (1913-14)
MOORE, C. H., 244, Fulwood Road, Sheffield .. .. (1917-18)
MOORE, CHRISTOPHER E,, The Hurst, Hagley, Stourbridge (1921-22)
MOORSHEAD, T.C., 40-43, Norfolk St., Strand, London, W.C.2. (1921-22)
MORFEY, H. A., The Shelton Iron Steel & Coal Co., Ltd., Stoke-on-Trent .. .. (1923-24)
MORETON WILLIAM P., c/o Messrs. Thos. Forrester & Sons, Ltd., Phœnix Works, Longton, Stoke-on-Trent .. .. (1921-22)
MORTON, JOSEPH, Ltd., Cinder Hill Fireclay Works, Halifax, Yorks. .. .. (1917-18)
MORRALL, F., 49, Kensington Road, Oakhill, Stoke-on-Trent (1917-18)
MOSS, G. H., 47, Heron Street, Fenton, Stoke-on-Trent .. (1920-21)
MOTTRAM, GEO. WM., Trevelyan Blgs., 52, Corporation Street, Manchester .. .. (1923-24)
MOULTON, D.A., Iowa State College, Dept. of Ceramic Engineering, Ames; Iowa, U.S.A. .. .. (1918-19)

MOURITZEN, C. F., Calyx Paint Works, Lord Street, Perth, Western Australia .. .. (1920-21)
MYERS, E. M., The Indian Iron & Steel Co., Ltd., Hirapur, Works, Asansol, E.I.R., Bengal, India .. .. .. (1921-22)
MYOTT, A., c/o Messrs. Myott, Son & Co., Cobridge, Burslem (1904-05)

NATIONAL MUSEUM OF WALES, Cardiff. .. .. .. (1924-25)
NAYLOR, BROS., Denby Dale, near Huddersfield .. .. (1924-25)
NEWBY, F. B., c/o Malkin Tile Works, Burslem, Staffs .. (1917-18)
NEWMAN, H. S., Sunnyside, Oxford Road, Basford Park, Stoke-on-Trent .. .. (1917-18)
NEWSOM, F. S., c/o Pountney & Co., Ltd., Fishponds, Bristol.. (1922-23)
NEW YORK PUBLIC LIBRARY, 476, Fifth Avenue, New York, U.S.A. .. .. (1921-22)
NICHOLSON, E. D., Park Issa, Oswestry .. .. .. (1918-19)
NIXON, WM., Mayfield, Weston Coyney, Stoke-on-Trent .. (1916-17)
NOBLE, E., Birch House, Worksop .. .. (1917-18)

OATES & GREEN, Ltd., Halifax, Yorks. .. .. .. (1916-17)
OAKES, W. c/o. Sand, Glass & Foundry Materials (Amalgamated) Ltd., 27, Waterdale, Doncaster .. .. .. (1920-21)
*ODELBERG, A.S.W., Gustafsberg Pottery, Gustafsberg, Sweden (1904-05)
OKURA, K., 22, Ipponmattsu, Azab, Tokyo, Japan .. .. (1915-16)
OLIVER, HAROLD, 6, Vicarage Road, Hartshill, Stoke-on-Trent .. .. (1924-25)
*OLSEN, B., The Villas, Stockton Brook, Stoke-on-Trent .. (1900-01)
ORMANDY, W. R., D.Sc., 18, Belsize Grove, Belsize Park, N.W.3. .. .. (1917-18)
OUGHTIBRIDGE SILICA FIREBRICK WORKS, The Oughtibridge, Sheffield .. .. (1916-17)

*PAGE, E. P., 123, Abbey Foregate, Shrewsbury .. .. (1904-05)
PAINE, J. W. R., Calder Fireclay Co., Coatbridge .. .. (1918-19)
PARKER, W. B., F.I.C., 3, Murray Road, Rugby .. .. (1918-19)
PARKINSON & SPENCER, Ambler Thorn Fireclay Works, Halifax .. .. (1916-17)
PARMELEE, C. W., Professor of Ceramic Engineering, University of Illinois, Urbana, Illinois, U.S.A. .. .. (1906-07)
PASS, R. H., West Rising, Onondaga Pottery Co., Syracuse, N.Y., U.S.A. .. .. (1920-21)
PEARSALL, W. H., c/o Mobberley & Bayley, Stourbridge .. (1916-17)
PEARSON, E. J. & J., Ltd., Fireclay Works, Stourbridge .. (1916-17)
PEARSON & Co., The Potteries, Whittington Moor near Chesterfield .. .. (1918-19)
PEASE & PARTNER, Ltd., Darlington .. .. (1923-24)
PENNY MAJOR, A. F., "The Elms," Park View Terrace, Worcester .. .. (1925-26)
PEREGRINE, C. R., C/o Macbeth-Evans Glass Company, Marion, Indiana, U.S.A. .. .. (1917-18)
PERRY, G. H. PEARSON, Portland House, Pedmore, nr. Stourbridge .. .. (1916-17)
*PERRY, T., Eastwood, Trentham Road, Penkhull, Stoke-on-Trent .. .. (1910-11)
PESCHERK, Dr., Breslau 16, Germany, Hansastr 1. .. .. (1924-25)
PICKFORD, HOLLAND & Co., Ltd., Eclipse Ganister Works, Attercliffe, Sheffield .. .. (1916-17)
PICKFORD, R. J., Etherley Lodge, near Bishop Auckland .. (1917-18)
PIKE, L. G., Wareham, Dorset .. .. (1912-13)
PILLAI, D. S., 39, Hill Street, Stoke-on-Trent .. .. .. (1923-24)
PINHEIRO DA SILVA, ISRAEL CARTHE, Minas Gerais, Brazil, South America .. .. (1920-21)

PITCAIRN, G., Fabrica-de-Loza, San Juan de Aznal-farache, Sevilla, Spain .. .. (1916-17)
PITT, NORMAN P., Oakfield, Brettell Lane, Stourbridge .. (1924-25)
PLANT, F., Stone Road, Longton .. .. (1912-13)
*PLANT, H. J., Rostherne, Park Avenue, Longton, Stoke-on-Trent .. .. (1902-03)
PLANT, J., Melbourne House, Stone .. .. (1912-13)
PODMORE, A. J., Consall Hall, Consall, Stoke-on-Trent .. (1916-17)
PODMORE, WM., Consall Hall, Consall, Stoke-on-Trent .. (1913-14)
POLGREAN, J. H., 183, Leek New Road, Burslem .. .. (1921-22)
POOLE, THOS., Cobden Works, Longton .. .. .. (1915-16)
POTTERY MANAGERS ASSOCIATION, A. E. Holdcroft, Sec., Woodland Avenue, High Lane, Burslem .. .. .. (1922-23)
POUNTNEY & Co., Ltd., The Bristol Pottery, Fishponds, near Bristol .. .. (1918-19)
POWELL, W. H., 41, Plymouth Street, Monteclair, New Jersey, U.S.A. .. .. (1908-09)
PRESTON, D., 35, High Street, Bucknall, Stoke-on-Trent .. (1916-17)
PRICE, G., Clifton, Milehouse Lane, Wolstanton, Staffs. .. (1908-09)
PRICE, J., Mount Cottage, Lawton, Stoke-on-Trent .. .. (1924-25)
PRICE, J. T. & Co., Ltd., Stourbridge .. .. (1916-17)
PRICE, S. H., "Lag-na-ha," Porthill, Stoke-on-Trent .. .. (1912-13)
PRYOR, E. A. COAD, 14, Hayesway, Beckenham, Kent .. (1917-18)

*RAMSDEN, C. E., Foley Colour Works, Fenton, Stoke-on-Trent (1902-03)
RAMSAY, A., Mount Savage, Md., U.S.A. .. .. .. (1908-09)
RANN, R. C., 17, Victoria Street, Westminister, London, S.W. 1. .. .. (1918-19)
REDFERN & DRAKEFORD, Balmoral Works, Normacot, Stoke-on-Trent .. .. (1918-19)
*REED, G. H., 71, Kershaw Avenue, Airedale, Castleford, Yorks (1921-22)
*REES, WALTER, J., Department of Refractory Materials, The University, Sheffield .. .. (1916-17)
RHEAD, F. H., Director, Research Dept., American Encaustic Tiling Co., Zanesville, Ohio, U.S.A. .. .. (1920-21)
RHEAD, T. F. E., 10, Malvern Road, Acocks Green, Birm'ham (1921-22)
REYNOLDS, G., Tachbroke House, Normacot.. .. .. (1903-04)
*RICHARDSON, A. G., "Linden," Oakville Avenue, High Lane, Burslem .. .. (1900-01)
RICHARDSON, GEO., 140, Pinnox Street, Tunstall
RICHARDSON, W. D., Schultz Building, Columbus, Ohio, U.S.A. (1906-07)
RIDGE, H. M., 2, Great Winchester Street, E.C. 2 .. .. (1917-18)
RIDGWAY, B. Bedford Works, Hanley .. .. (1913-14)
RIDGWAY, F. J., H. Aynsley & Co., Commerce Street, Longton, Stoke-on-Trent .. .. (1921-22)
RIES, H., Cornell University, Ithaca, New York .. .. (1911-12)
RIGBY, A., St. Anthony's Drive, Newcastle, Staffs. .. (1920 21)
RIGBY, J. H., Buccleuch Road, Longton .. .. .. (1921-22)
ROBERTS, J. G., c/o Messrs. Shanks & Co., Barrhead, N.B. (1904-05)
ROBERTS & MAGINNIS, Ltd., Trevor, Ruabon, N. Wales .. (1921-22)
ROBINSON, H. T., China Works, Shelton, Stoke-on-Trent .. (1917-18)
ROBINSON, P. B., 20, Aynsley Terrace, Consett, Co. Durham.. (1922-23)
ROBERTSON, N. L., Dregham, Tanfield Road, Blowers Green, Dudley .. .. (1922-23)
ROSS, DONALD W., The Findlay Clay Pot Co., Washington, Pa, U.S.A. .. .. (1917-18)
ROYCE, Miss F. A., 24, McKillop Street, Geelong, Victoria .. (1922-23)
ROWLAND, B. R. & Co., Ltd., Climax Works, Reddish, nr. Stockport .. .. (1923-24)
ROWLEY, T. H., 63, Gilman Street, Hanley .. .. .. (1921-22)

*RUSSELL, FRANK, Auldam House, Worksop .. .. .. (1916-17)
SADLER, EDWARD, Newlands, Watlands Avenue, Wolstanton (1917-18)
SAILLY, PAUL, Compagnie Générale d'Electro-Céramique, 64, Rue Franklin, Ivry-Port, Seine, France .. .. (1917-18)
SALT, F., Central School of Science, Stoke-on-Trent .. .. (1922-23)
SANITER, E. H., Phoenix Special Steel Works, The Ickles, Sheffield .. .. (1916-17)
SANKEY, C. H., Wildcroft, Chislehurst, Kent.. .. .. (1916-17)
SATOH, SHINZO, Esq., Tokio Electric Co., Ltd., Kawaski, Kanagawa-Ken, Japan.. .. .. (1920-21)
SAXTON, C., 35, Bedford Street, Strand, London, W.C., 2 .. (1918-19)
SAYER, JAMES, Junr., Hill Crest, James St., Stoke-on-Trent (1912-13)
SCHURECHT. H. G., 5327, 41st Street, N.W., Washington, D.C., U.S.A. .. .. (1922-23)
SCRIVENER, E. D., c/o Messrs. Taylor, Tunnicliff & Co., Eastwood, Hanley .. .. (1908-09)
*SCOTT, A., M.A., D.Sc., Central School of Science and Technology, Stoke-on-Trent .. .. (1917-18)
*SEARLE, A. B., The White Building, Sheffield.. .. .. (1907-08)
*SHAH, C. P., Nadiad, B.B.C.I. Ry., India.. .. .. .. (1913-14)
SHANKS, D., Raisdale, Barrhead, N.B. .. .. .. (1905-06)
SHAW, A. G., Whitebrick Brick Works, Darwen, Lancs. .. (1918-19)
SHAW, RITCHIE, Fylands Fireclay Works, Bishop Auckland, Co. Durham .. .. (1922-23)
SHELLEY & Co., Foley China Works, Fenton, Stoke-on-Trent (1921-22)
SHENTON, E., Wedgwood & Co., Tunstall .. .. .. (1924-25)
SHERLOCK, A., Winterton Pottery, High Street, Longton .. (1916-17)
SHIRLEY, T. H. F., Walton Lodge, Stone, Staffs. .. .. (1921-22)
SIEURIN, E., Höganas, Sweden .. .. (1922-23)
SILLARS, D., Bidston, Britannia Terrace, Saltburn-by-the-Sea (1918-19)
SIMPSON, T. A., The Limes, Sunny Bank Road, Newcastle-under-Lyme .. .. (1914-15)
SIMPSON, T. G., 34, Elm Street, Cobridge, Stoke-on-Trent.. (1917-18)
SIMPSON, W. A., 27, Kensington Rd, Oakhill, Stoke-on-Trent (1916-17)
SIMPSON, E., 35, Pynest Street, Shelton, Stoke-on-Trent .. (1918-19)
SINGER, Dr., Felix, Charlottenburg 2 Carmerstr. 18 .. (1924-25)
SINGH KRISHEN, Katni Cement Factory P.O. (C.P.) India .. (1921-22)
SMITH, H. PROCTER, Hawarden Bridge Steel Works, Shotton, Chester.. .. .. (1916-17)
SMITH, OLIVER, Lilac House, Hunwick, Willington, Co. Durham .. .. (1916-17)
SMITH, F.R., Eastfield, Ironbridge, R.S.O., Salop .. .. (1902-03)
SNEYD COLLIERIES, Ltd., Burslem .. .. (1916-17)
SNOW, WILFRED, R., G.P.O. Box No. 525, Adelaide, South Australia .. .. (1918-19)
SOCIETIE DES PRODUITS CERAMIQUES ET REFRACTARIES, 4, Rue Blanche, Paris .. .. (1918-19)
SOHO POTTERY Ltd·, Elder Works, Cobridge, Stoke-on-Trent (1921-22)
SOMERVILLE, W., The Cottage, Hindlow, Buxton
SOSMAN, R. B., 2801, Upton Street, Washington, D.C., U.S.A. .. .. (1918-19)
SOUTH METROPOLITAN GAS Co., 709, Old Kent Road, London, S.E. 15 .. .. (1917-18)
SPEIRS, C. W., The Morgan Crucible Co., Battersea Works, London .. .. (1916-17)
SPROAT, IRA E., c/o R. T. Vanderbilt & Co., 50, East 42nd Street, New York, U.S.A. .. .. (1923-24)
STALEY, HOMER F., Metal and Thermit Corporation, 120, Broadway, New York .. .. (1924-25)
STANLEY BROS., Ltd., Brick Works, Nuneaton .. .. (1922-23)

STANLEY, CYRIL .. .. (1921-22)
*STANLEY, WALTON, Station Hotel, Stoke-on-Trent .. .. (1911-12)
*STANYER, A., 24, Jenkins Street, Burslem .. .. .. (1903-04)
STANWAY, P. W., Clive House, Clive Street, Shelton .. (1921-22)
STATON, A. D., 37, King's Avenue, Wolstanton, Stoke-on-Trent .. .. (1920-21)
STEELE, H. L., Messrs. The Britannia Pottery Co., Ltd., 136, Glebe Street, St. Rolox, Glasgow .. .. (1912-13)
STEIN, JOHN G. & Co., Ltd., Bonnybridge, Scotland .. (1916-17)
STEIN, JOHN G., Millfield, Polmont, Scotland .. .. .. (1923-24)
STEIN, Col. ALLAN, Glenbervie, Larbert, Scotland .. .. (1923-24)
STEPHENS, ALFRED, Sir, Broomhill, Kidwelly .. .. (1916-17)
STEVENSON, H. W., Royal Pottery, Burslem .. .. (1913-14)
STEVENSON, SAMUEL, 59, Elm St, Cobridge, Stoke-on-Trent (1921-22)
STOTT, VAUGHAN H., 9, Elmers Drive, Teddington, Middlesex.. .. .. (1920-21)
STOTT, C., Benroyd, Holywell Green, near Halifax .. .. (1923-24)
STOURBRIDGE REFRACTORIES Co., Ltd., Pensnett, nr. Dudley .. .. (1916-17)
STOURBRIDGE FIREBRICK TRADE (Secretary, Mr. Wm. Fullwood), Church Street, Chambers, Stourbridge.. .. (1923-24)
STOVER, E., 474, West State Street, Trenton, U.S.A. .. (1903-04)
STRINGER, G. E., Wynberg, Newcastle Road, Stone, Staffs. (1918-19)
STUBBS, R., 8, The Avenue, Blythe Bridge .. .. .. (1920-21)
SUR, M. M., 65/2, Serpentine Lane, Calcutta .. .. .. (1922-23)
SUTHERLAND, W. FRANK, 79, Normandy Buildings, Toronto, Ont., Canada .. .. (1918-19)
SWIFT & NETHERWOOD, Lepton, Fenay Bridge .. .. (1921-22)
SWINNERTONS, Ltd., Vulcan Pottery, Hanley, Stoke-on-Trent (1918-19)
SYLVANY, R., Managing Director of E.I.C.T, 78, Rue d'Anjou Paris, 8 .. .. (1925-26)

TARRANT, W. G., Ltd., Byfleet, Surrey .. .. .. (1921-22)
TAYLOR, F. E., Trentham, Staffs. .. .. (1913-14)
TENNANT, J., Hawthorne Street, off Holly Lane, Warrington (1954-26)
THE ARMITAGE WORKS Co., Ltd., Deipcar, nr. Sheffield .. (1925-26)
THEOBALD, L. S., c/o Mrs. Williams, 3, Ennismore Avenue, Chiswick, London, W. 4. .. .. (1923-24)
THOMAS, C. W., c/o Messrs. E. J. & J. Pearson, Ltd., Brierley Hill, S. Staffs. .. .. (1903-04)
THOMAS, C. A. G., Clifton House, Old Swinford, Stourbridge (1921-22)
*THOMASON, W., Hindleshaw, Nelson Road, New Malden .. (1909-10)
THOMPSON, H. H., 52, Lombard Street, Birmingham.. .. (1921-22)
THOMPSON, J. H., The Vicarage, Leek, Staffs... .. .. (1922-23)
THORLEY, J. P., "Glenelg," Victoria Road, Newcastle.. .. (1923-24)
THRELFALL, C. R. F., c/o Timmis & Co., Stourbridge .. (1920-21)
THURSFIELD, W. T., Hillcrest, Greeenbank Road, Burslem (1921-22)
TIDY, CHARLES J., c/o The Cemaes Brick & Tile Works, Cemaes Bay, Anglesey .. .. (1921-22)
*TIMMIS, G. H., Storrage House, Wribbenhall, Bewdley .. (1916-17)
TOOGOOD, H. J., The Poplars, Elland, Yorkshire .. .. (1918-19)
TOOTH, W. E., Claridge House, Woodville, Burton-on-Trent (1913-14)
*TOWNSEND, H., Mount Avenue, Hartshill, Stoke-on-Trent (1909-10)
TREDDENICK, WM., 3, Primrose Hill, Newfield, Willington, Co. Durham .. .. (1921-22)
TROOP, R. S., 305, Princes Road, Hartshill, Stoke-on-Trent .. (1923-24)
*TURNER, F., Cranleigh, Brampton, Newcastle .. .. (1900-01)
TURNER, Prof., W. E. S., D.Sc., Department of Glass Technology, The University, Sheffield .. .. (1916-17)
TWYFORDS Ltd., Cliffe Vale Potteries, Hanley, Stoke-on-Trent (1923-24)

UNITED COLLIERIES, Ltd., 109, Hope Street, Glasgow .. (1916-17)
UNIVERSITY OF WASHINGTON LIBRARY, Seattle, Washington .. .. (1920-21)
UNIVERSITY OF CALIFORNIA LIBRARY, Berkley, California, U.S.A. .. .. (1920-21)

VERZOCCHI, G. Corso Italia 1, Milan, Italy .. .. .. (1923-24)
VIGGARS, G. H., The Villas, Silverdale, Staffs... .. .. (1922-23)
*VICKERS, A. E. J., 27, Lily Street, Wolstanton, Stoke-on-Trent .. .. (1918-19)

WADE, G., High Street, Burslem .. .. (1914-15)
WAGNER, W. G., c/o George T. Holloway & Co., Ltd., 13, Emmett Street, Limehouse, London, E. 14.. .. .. (1922-23)
WAGNER, B. F., C/o The Coonley Manufacturing Co., Cicero, Ill., U.S.A. .. .. (1923-24)
WAGSTAFF, J. J., 51, Oulton Road, Stone .. .. .. (1921-22)
WALKER, E. E., The Australian Tesselated Tile Co., Ltd., Mitcham, Victoria, Australia .. .. (1916-17)
WALKER, F. W., Art Tile Works, Beaver Falls, Pa, U.S.A. (1906-07)
WALKER, JOHN, Ltd., Oak Farm Works, Kingswinford, nr. Dudley .. .. (1916-17)
WALTON, C. J., Forsbrook, Stoke-on-Trent .. .. .. (1912-13)
WARBURTON, T. H., The Monk Bridge Iron & Steel Co., Ltd., Leeds .. .. (1916-17)
WARD, T. W., Endcliffe Vale House, Sheffield .. .. (1917-18)
WATERHOUSE, JAMES, Ltd., Soho Works, Wakefield .. (1916-17)
WATTISON, J. T., Rua Candid dos Reis 103, Oporto .. .. (1918-19)
*WATKIN, E., Greyholme, The Greenway, May Bank, Stoke-on-Trent .. .. (1916-17)
WATTS, A. S., Lord Hall, O.S.U., Columbus, Ohio, U.S.A. .. (1910-11)
WEATHERLEY, W. H., c/o. C. Tennant, Sons & Co., Ltd., 80/82, Merchant's Exchange, Cardiff .. .. .. (1924-25)
WEBSTER, J. C., Bridge Pass, Victoria Road, Tunstall .. (1910-11)
WEBSTER, JAS., Lynve, Victoria Road, Tunstall .. .. (1913-14)
WEDGWOOD & Co., Tunstall .. .. (1924-25)
WEDGWOOD, Miss A., The Woodhouse, Cheadle, Staffs. .. (1916-17)
*WEDGWOOD, F. H., c/o Josiah Wedgwood & Sons, Ltd., Etruria, Stoke-on-Trent .. .. (1905-06)
WELLINGTON GAS Co., Courtney Place, Wellington, N.Z.
WELLS, J. H., 10, Glanbrydan Avenue, Uplands, Swansea.. (1916-17)
WENGER, A. H., Trentham Priory, Staffs. .. .. .. (1902-03)
WENGER, F. E., The Hollies, The Brampton, Newcastle Staffs (1905-06)
*WENGER, T. L., Victoria House, London Road, Newcastle .. (1922-23)
WERNER, E. A. R., 174, Corporation Street, Birmingham.. (1920-21)
WERNER, EDWARD, Warsaw al. Ujazdowska 36 .. .. (1924-25)
WEST COAST PORCELAIN MFGS., Millbrae, California, U.S.A. (1923-24)
WESTS GAS IMPROVEMENT Co., Ltd., Albion Iron Works, Miles Platting, Manchester .. .. (1923-24)
WHISTON, H. W., 12, Hollings Street, Fenton, Stoke-on-Trent (1920-21)
WHALLEY, G. 8, Forster Street, Tunstall .. .. .. (1924-25)
WHITE, G. J. C., 290, Princes Road, Penkhull, Stoke-on-Trent (1924-25)
WHITELEY, A., 7, Glen Road, Netheredge, Sheffield.. .. (1917-18)
WHITELEY, J. H., 11, Cambridge Street, Saltburn, York. .. (1918-19)
WHITFIELD, T. S., c/o The Cobridge Brick Co., Burslem .. (1905-06)
WIDEMANN, R. V. E., 30, Rue des Dames, Paris (xvii.) .. (1922-23)
WILD, ARTHUR, Hawthorn Dene, Hathersage .. .. (1916-17)
WILKINSON & SONS, S., Blackley Fireclay Works, Elland Yorks. .. .. (1916-17)
WILKINSON, A. J., Ltd., Burslem, Stoke-on-Trent .. .. (1922-23)

WILLIAMS, C. P., M.Sc., Flwdwycet, Penrycae, Port Talbot (1916-17)
WILLIAMS, F. R., 1, Beaconfield Villas, Brighton .. .. (1902-03)
*WILSON, S. T., Park Works, Fenton, Staffs. .. .. .. (1904-05)
WILSON, L. M., Whiteley Wood, Sheffield .. .. .. (1923-24)
WILTSHAW & ROBINSON, Carlton Works, Copeland Street, Stoke-on-Trent .. .. (1916-17)
WINKLE, L. H., Colonial Pottery, Stoke-on-Trent .. .. (1908-09)
WINNICOTT, A. B. (Mrs.), 89, Ditton Hill Road, Surbiton, Surrey .. .. (1918-19)
WOOD, A. R., c/o Pilkingtons, Ltd., St. Helens, ... (1920-21)
*WOOD, H. E., Hillside, Hamil Road, Burslem.. .. : (1900-01)
WOOD, H. F., The Uplands, Brampton, Newcastle, Staffs. .. (1911-12)
WOOD, ROBERT, Quarry House, Dudley, Worcestershire .. (1921-22)
*WOOLDRIDGE, F., Taylor, Tunnicliff & Co., Hanley .. (1905-06)
WOODWARD, H., Prince of Wales Works, Sutherland Works, Longton .. .. (1925-26)
*WORTHINGTON, F. S., 2, Grove Place, Shelton, Hanley .. (1907-08)
WRAGG, THOS., & SONS, Storrs' Fireclay Works, Loxley, near Sheffield .. .. (1916-17)
WRAGG, THOS., & SONS, Swadlincote.. .. .. .. (1917-18)
WRIGHT, J. E., 153, Cauldon Road, Hanley .. .. .. (1914-15)
WRIGHT, W. T. & Co., Ltd., Sileby, near Loughboro' .. (1921-22)

The numbers in brackets denote the session of election.

Any change of postal address should be communicated to the Assistant Secretary,

A. RIGBY, Pottery Laboratory, Stoke-on-Trent.

Student Members.

ASH, S., West End, Church Square, Burslem .. .. .. (1922-23)

CHAMBERS, A., "Littlewood" Worsley, Manchester .. .. (1924-25)
CATER, A., Manse, High Lane, Burslem .. .. .. (1924-25)

FOSKETT, W., 7, Derby Street, Burslem .. .. .. (1924-25)

HANCOCK, N., 138, Dimsdale Parade, Wolstanton .. .. (1924-25)
HEAP, J. W., 9, Morley Street, Tunstall.. .. .. .. (1920-21)

JONES, A. G., 14, Boulton Street, Birches Head, Hanley .. (1923-24)

MANSHARAMANI, G. T., 3, Stone Road, Longton .. (1924-25)
MEREDITH, W. D., New Villas, Shirley Road, Hanley .. (1925-26)

PADDOCK, G. J., "Coatbridge" Basford .. .. .. (1924-25)

RICHARDSON, W. F., 15, Rectory Road, Shelton, Stoke-on-Trent .. .. (1925-26)
RIGG, J. F., 27, Gordon Street, Hartshill, Stoke-on-Trent .. (1925-26)

STEVENSON, J. H., 125, Dimsdale Parade, Wolstanton .. (1923-24)
SHAW, W. F., 48, Albert Street, Sandford Hill, Longton .. (1924-25)

Proceedings.—Session 1924-25.

The opening meeting of the session was held on Monday, 6th October, 1924, in the Central Science School. The President, Mr. A. G. Richardson, occupied the chair. The attendance was 115. Apologies for absence were received from: Dr. J. W. Mellor, Mr. T. A. Simpson, and Mr. J. Holland. Nominations for membership were received on behalf of the following:—Signor G. Verzocchi, Mr. J. H. Harrison; and as a Student Member, Mr. W. Hancock. The following papers were given by Mr. A. S. W. Odelberg: (1) "More about the Dorr Mill"; (2) "The Swedish Felspar Industry"; "The Society's Italian Excursion." Questions were asked by Mr. A. G. Richardson, Mr. B. J. Moore and Mr. C. E. Ramsden.

General Meeting held in the Central Science School, Stoke-on-Trent, on Monday, 10th November, 1924. Mr. A. G. Richardson presided over an attendance of 85 members. An apology for absence was received from Mr. G. Price. Dr. F. Singer, Berlin, was proposed for membership. The President moved a vote of sympathy with the relatives of the late Mr. Robt. Shenton and Mr. J. G. Aynsley. Mr. Harold J. Plant read a paper on: "Pinholes and some other things," and a long discussion followed which brought the meeting to a close.

General Meeting held in the Central School, Stoke-on-Trent, on Monday, 8th December, 1924. There was an attendance of about 56 and Mr. B. J. Moore presided. Apologies for absence were received from: The President, Mr. T. Bates and Mr. D. W. F. Bishop. The following were proposed for membership: Ordinary: Mr. Brittain Adams, Jnr.; Student: Messrs. G. F. Mansharamani, G. J. Paddock, R. A. Green, W. F. Shaw, A. Chambers. A vote of sympathy was passed with the relatives of the late Mr. T. W. Owen. A paper was given by Mr. F. Lane entitled: "Notes on Crushing and Grinding Mills."

General Meeting held on Monday, 12th January, 1925, in the Central School of Science, Stoke-on-Trent. Chairman: The President. About 65 members were present. Proposals for membership were received from: Mr. D. V. Hollingworth, Mr. B. Mellor, Mr. W. Emery (Hanley) as Ordinary Members; Mr. C. J. Cater as a Student Member. Apologies for absence were received from Mr. H. J. Plant and Mr. T. A. Simpson. The meeting took the form of a Question Box and the following questions were discussed; "What are the principal causes of whirler plates ?" Answered by Mr. E. Gleaves. "In the case of art ware have the alkalies as used in casting slips any relation to the flashing caused in biscuit firing ? Would the same result be got without the use of alkalies ?". Answered by Mr. W. Emery. "What is the

cause of a light cobalt blue, printed on biscuit, turning milky through the glost oven ?" Answered by Mr. S. Ash. "Is it likely that sillimanite can be used in place of bedding flint with any advantage to the worker from the dust point of view ?" Answer communicated by Mr. H. J. Plant. "Which is the best test for crazing—the salt pot or superheated steam ?" Answered by Mr. C. D. Grimwade.

General Meeting held on Monday, 9th February, 1925, in the Central Science School, Stoke-on-Trent. Mr. A. G. Richardson presided. 48 members were present. Apologies for absence were received from Mr. F. S. Worthington and Mr. G. Price. The Chairman announced that the portrait of Mr. Bernard Moore had been hung in the School Museum. Proposals for membership were received on behalf of the following: The National Museum of Wales, Mr. T. E. Werner (Warsaw), Mr. E. Shenton, Dr. Pucheok (Breslau) and Mr. W. F. Richardson, the last named as a Student Member. Mr. W. Emery communicated by title a note entitled: "Notes on Whieldon Pottery." A vote of sympathy with the relatives of the late Mr. Stephen Hawthorne was passed. Mr. S. R. Hind, B.Sc., read a paper entitled: "Visit to the Osmosis Plant at Carlsbad," and in the subsequent discussion the speakers were Messrs. B. J. Moore, A. Rigby, C. D. Grimwade, E. E. Eley and R. F. Bullock. Mr. C. Reynolds described and demonstrated an Enamel Tile Dipping Machine.

Open meeting held on Wednesday, 4th March, 1925, in the Central Science School. The Chair was taken by the President and the attendance was 85. Dr. E. L. Middleton read a paper entitled: "Demonstration of Dust Counting as applied to the Estimation of Injurious Dusts in Potters' Shops." The following contributed to the discussion: Dr. Mellor, Mr. J. Burton and Sir Thomas Legge. An apology for absence was received from Mr. A. E. R. Werner.

General Meeting held on Monday, 6th April, 1925, in the Central Science School. Mr. A. G. Richardson presided over an attendance of about 40. Proposals for membership were received from: Societa Ceramica Richard Ginori (Milan), Naylor Bros., Laclede-Christy Clay Products Co. (St. Louis), California Pottery Co. (San Francisco); A. E. Jones & Co., N. P. Pitt, F. Wheeler, W. Marshall. Apologies for absence were received from: Major F. H. Wedgwood, Dr. J. W. Mellor and Mr. T. G. Simpson. A Note by Dr: J. W. Mellor referring to Dr. Martin's paper on surface factors was taken as read. Mr. W. Emery read a paper entitled: "Notes on Whieldon Pottery" which was followed by a discussion in which the following took part: The President, Messrs. H. Barnard, A. Heath and T. Pape. "A Note on Frit Kilns" was read by Mr. S. R. Hind, B.Sc. and Messrs. A. Heath, C. D. Grimwade, J. Meredith, F. Turner and B. P. Codling contributed to the discussion.

Annual Meeting held on Monday, 11th May, 1925, in the Central Science School, Stoke-on-Trent. Mr. A. G. Richardson presided over an attendance of about 35. Nominations for membership were received from Mr. G. Perrins, Mr. H. Oliver. The election of officers for the session 1925-26 resulted as follows: Vice-President: (elected for 3 years), Mr. B. J. Moore; Council representatives: Messrs. G. Campbell, F. Turner, A. Heath and G. Allman (elected for 3 years); Auditor: Mr. B. J. Allen. A vote of thanks to all the Officers for the session 1924-25 was passed unanimously. Councils' Annual Report was read and adopted. The retiring President—Mr. A. G. Richardson—gave an address, and the meeting closed with a very hearty vote of thanks to Mr. Richardson for his services to the Society.

Proceedings of the Refractory Materials Section of The Ceramic Society.

General Meeting held on Thursday and Friday, 18th and 19th September, 1924, in Conference Hall 4, British Empire Exhibition, Wembley. Chairman—J. Holland, Esq. On Thursday morning the following papers were read: "A Comparison of Gas and Coke-fired drying Stoves together with a Description of the Construction and Operation of the Hüttenes Coke Fired Air Blown Furnace" by Mr. Thos. W. Barley; "Some Properties of Clay Sillimanite Mixtures" by Mr. H. S. Houldsworth, B.Sc.; "The Influence of Exposure on the Chemical and Physical Properties of certain Fireclays" by Mr. W. Hugill, M.Met., and Mr. W. J. Rees, B.Sc., F.I.C. The afternoon session was devoted to the business of the Society. Apologies for absence were received from: Dr. J. W. Mellor, Mr. G. R. L. Chance, Col. A. Stein, Col. C. W. Thomas, Sir Wm. Jones, The Lilleshall Company, Mr. H. T. Arrowsmith, Mr. H. S. Houldsworth and Mr. Bernard Moore. Nominations for membership were accepted on behalf of the following: Collective: Messrs. G. Mellor & Co. Ltd., Messrs. R. S. Troop, Reginald Till and J. N. Bell. As the Council had not met since the last election, the district representatives were re-elected en bloc. Mr. J. Holland proposed a very hearty vote of thanks to the authorities of the British Empire Exhibition for the use of the Conference Hall and Committee Room and Dr. Colman seconded.

On Friday the following papers were read: "Alumina-Silica Minerals in Firebricks," "Note on the Storage of Silica Refractories"; "The True Specific Gravity and After-Expansion of Lime-bonded Silica Bricks" by Mr. W. J. Rees, B.Sc.; "The Action of Heat on Kaolinite and other Clays, Part II." by Dr. J. W. Mellor

and Dr. A. Scott, M.A.; "The Origin of the Austrian Magnesite Deposits" by Dr. A. Scott; "The X-Ray Investigation of Clays and other Ceramic Substances. Researches into the Application and the Practical Value of the Method" by Mr. Assar Hadding (Sweden); "A Rapid Method for the Determination of True (or powder) Specific Gravity" by Mr. W. Hugill, M. Met., and Mr. W. J. Rees, B.Sc. Discussions on the above papers brought the meeting to a close.

General Meeting held on Tuesday, 19th May, 1925, in the Palace Hotel, Buxton. This meeting was the opening session of the first Clayworkers' Convention to be held in this country. Apologies for absence were received from: Mr. H. Wragg, M.P., Dr. G. H. Colman, Mr. W. T. Gardner, Mr. T. A. Acton, Mr. H. E. Mason, Mr. G. V. Evers and Mr. G. R. L. Chance. The following were appointed to represent the new district (North Yorkshire, Northumberland and Durham) Mr. C. Gregory, Mr. A. H. Middleton and Mr. R. J. Pickford. A vacancy was declared in the Sheffield district. Mr. F. West was elected President of the Society. Sir Wm. Jones proposed a vote of thanks to the retiring President, Mr. J. Holland, which Dr. Mellor seconded. The resolution was passed with enthusiasm. Mr. W. Hamilton was elected an auditor of the Society. Mr. J. Holland proposed a vote of thanks to the Clay Convention Committee and the Derbyshire Silica Firebrick Company for their kind assistance in arranging the meeting at Buxton. Mr. West seconded and the meeting heartily approved of same. The following papers were given: "Insulation of Ovens and Kilns" by Mr. A. T. Green; "The effect of Repeated Burning on the Properties of Silica Bricks" by Mr. W. J. Rees, B.Sc. The following were taken as read: "Manufacture of Magnesite" by Mr. G. H. Reed; "A Note on the Structure of a Fused Fireclay Crucible" by Mr. W. J. Rees. During the afternoon the following papers were taken as read: "The Effect of Iron Oxide on the Rate of Inversion of Quartz"; "Observations on the Elimination of Carbonaceous Matter from Fireclay Bricks" by Mr. L. S. Theobald, B.Sc., A.R.C.S., and Mr. A. T. Green; "An Investigation of the Change taking place during the Industrial Burning of Fireclay Bricks" by Mr. A. T.Green and Mr. L. S. Theobald, B.Sc. A paper was also read by Mr. T. F. E. Rhead and Mr. R. E. Jefferson on "Notes on (1) Testing of Refractoriness and After-Contraction; (2) A few Experiences with Refractories in Vertical Retorts." Mr. W.Boyd Mitchell and Mr. J. Mitchell gave a paper on "Molybdenum Wound Furnace" and a discussion on the above brought the meeting to a close.

Council's Annual Report.

In this our 24th Annual Report there are few striking incidents to record, but the general interest in the Society has been well maintained. At the present time the membership list stands as follows :—

Honorary	6
Individual	568
Collective	109
Student	14
Total ..	697

We regret to have to put on record that we have lost by death Mr. Robert Shenton a past-president of the Society, Mr. Stephen Hawthorn, Mr. J. G. Aynsley and Mr. T. W. Owen.

Papers covering a wide range of subjects have been read at the usual monthly meetings at Stoke-on-Trent, while the Refractory Materials Section had a most successful meeting at Wembley in the Autumn of 1924.

During the past session the members of the Society, assisted by many outside friends placed a commission with Mr. Oswald Birley, to paint a portrait in oils of Mr. Bernard Moore. Mr. J. V. Goddard acted as Secretary for this particular effort and the work has been completed. At a meeting of the subscribers held on Tuesday, 28th October, 1924, it was decided that the portrait should be placed in the charge of three trustees and the following were appointed :—

President of The Ceramic Society.

President of the British Pottery Manufacturers' Federation.

Chairman of the Governors of the Central School of Science and Technology.

The trustees arranged for the portrait to be hung in the Central School of Science. A replica of the portrait was presented to Mr. Moore at a Dinner held in his honour on November 18th, 1924.

We regret to record that Mr. H. Townsend, after many years valuable service as Reporter, tendered his resignation during the session. This was accepted with regret.

Our grateful thanks are due to the Governors of the Central School of Science, Stoke-on-Trent, for the use of rooms during the session, and to the authorities of the British Empire Exhibition, Wembley, for the use of Conference Hall and Committee room.

B. J. MOORE,
Chairman.

Stoke-on-Trent, 11th May, 1925.

CERAMIC SOCIETY.

Statement of Account for Session 1924-25.

Income.	£	s.	d.
Balance in hand Session 1923-24	173	15	8
Firms' Subscriptions ..	216	6	0
Members' ,, ...	595	4	8
Students' ,, ...	4	0	0
Advertisement Dept. ..	331	7	0
Transactions sold	231	7	1
Postages paid	13	2	3
Bank Interest	6	6	6
Unpresented cheques ..	5	18	9
Sundries	18	8	0
	£1595	15	11

Expenditure.	£	s.	d.
Printing Transactions ..	804	17	9
Blocks for Transactions ..	35	4	10
Journals	51	10	9
Expenses of Meetings ..	47	3	6
Postages	96	10	5
Reporting	1	2	6
Printing and Stationery ..	64	14	1
Binding Transactions, etc.	17	5	3
Governors of Central School of Science	50	0	0
Insurance	3	17	6
Bank Charges	1	11	6
Cheque Books		10	0
Honorariums	57	0	0
Sundries	9	19	0
Unpresented cheques, 1923-24	1	0	6
Balance in hand, 1924-25 ..	353	8	4
	£1595	15	11

Against the Balance of £353 8s. 4d., there are debits owing for about £250 to complete the Statement of Account for Session 1924-1925.

Audited and found correct, November 27th, 1925.

Signed by B. J. Allen.

J. Meredith.

I.—A Comparison of Gas and Coke Fired Drying Stoves;

together with a Description of the Construction and Operation of the Oehm Heating Unit.

By T. W. Barley.

THE subject of this paper has a special interest for the Iron and Steel Founder and equally so, I am advised, for the Manufacturer of Ceramics.

The continuous advance in the price of fuel together with a contracted market for the finished steel product compels attention to every possible means of effecting economies in the consumption of fuel, one of the heaviest items of expenditure in the production of steel.

The cost of drying moulds and cores at the Imperial Steelworks of Messrs. Edgar Allen & Co., Ltd., Sheffield was, amongst a number of other subjects, selected for analysis and this paper will, in general terms, describe the researches carried out and the deductions derived therefrom.

In a steel or iron foundry, it is necessary to dry a portion of the moulds and cores, such dried moulds and cores being known technically as "dry sand work" in contradiction to undried or "green sand work." Many of the moulds and cores are of considerable dimensions and a further difficulty, from the point of view of drying, is, that the moulds are contained in thick cast iron or steel boxes.

It is obvious therefore, that the problem demanding solution presents difficulties, especially as the time in which the operation must be completed is strictly limited. In the Imperial Steelworks the time available is from 5 p.m. to 8 a.m., a period of 15 hours.

When I first became acquainted with the Imperial Steelworks, some 16 or 17 years ago, the mould drying was carried out by loading the moulds on to a large carriage or bogie, which was drawn into a brick chamber, provided with fire-boxes at the end farthest from the door, and constructed to burn coke. The process was very unsatisfactory, large quantities of coke being consumed; some of the moulds were spoilt by overheating, others were not sufficiently dried and had to be returned, and a proportion only was in a suitable condition to permit of casting; however, such was the system in general practice, not only at the Imperial Works, but elsewhere. I have reason to think that, even to-day, this method is still in use in some foundries in this country. To illustrate the wasteful use of fuel in a furnace of this design, it will be suf-

ficient to say that a drying stove of only 710 c.ft. contents required 17 cwts. of coke per 14 hours.

However, in 1911, it was decided to rebuild our foundry. The amount of land at our disposal was limited, and it was imperative that every yard of it should be used to the very best advantage; this, together with the recognised inefficiency of the coke-fired stoves led to careful enquiries and search for better methods. As a consequence, it was decided to lay down a number of drying chambers operated by Sheffield town's gas, which at this time was both very cheap and of very good quality.

The reasons for this decision were (1) the whole of the available space could be used for the drying chamber; no room being required for the furnace; (2) The construction could be simplified and, therefore, cheapened; (3) No chimneys were necessary; (4) At the time the price of gas was 10d. per 1,000 for gas at about 560 B.T.Us., and by the elimination of all carting both for fuel and ashes, and the possibility of reducing the number of attendant operators, it was considered that the use of gas would actually effect a reduction in costs. This proved to be the case, but the war broke out shortly after the new foundry commenced working, and arising out of this, the price of gas advanced whilst the quality receded; further, the Gas Company reduced the pressure to an extent that made it impossible to keep the burners alight and booster fans were installed to raise the pressure.

However, little could be done to deal with the extraordinary increase in costs until after the conclusion of the war, when the whole question was carefully investigated.

You will, of course, appreciate that, whilst the war was in progress, no opportunity presented itself for other considerations but those of increasing output, and, therefore, although it was realised that gas-fired drying stoves left something to be desired, they performed their work, and, compared with the old coke-fired furnaces, possessed undoubted advantages, amongst others the minimum amount of labour sufficed for working, a very important consideration indeed during this period.

However, when the "Industrial Slump" arrived with us it was imperative, to carry on at all, that all items of expenditure should be strictly investigated, and, amongst others, the drying problem, as it had come to be known, received close attention.

It will help us to obtain the proper perspective to mention that, in 1915, we consumed 76,615,500 cubic feet of gas for drying, for which we paid £3,939 0s. 0d., whilst in 1920, for 53,619,900 cubic feet, we paid £9,691 0s. 0d., a decrease of 22,995,600 cubic feet in the consumption, but an increase of £5,562 0s. 0d. in the price paid.

In the first place, the drying chambers are plain rectangular constructions varying in size, the standard size being 25′ 0″ × 11′ 6″ × 7′ 6″ high. The gas burners are of standard bunsen type

arranged along the back in most instances, three chambers only being fitted with burners down each side, thermostatic valves in every case being installed, which, however, proved to be quite valueless.

Of course the first procedure to be adopted in conducting a research of this nature is to ascertain, as exactly as possible, the existing conditions and working procedure.

Our first enquiries were directed to the working temperature, but it was found that considerable diversity of opinion existed, not only as to the actual temperature attained in the stoves, but the temperature necessary to effect drying. No thermometers had been fitted and the foreman in charge employed the device of spitting on the outside of the doors to judge the degree of heat, presumably by the speed of evaporation.

Obviously the first thing to be done was to fit up thermometers, and one of Negretti & Zambra's recording instruments was fitted, and in the meanwhile a separate gas meter was attached to a standard stove together with a gas regulator, so as to be able to maintain a constant gas pressure at any desired water gauge within the limits of the mains pressure, which we had found to be a variable quantity. The thermometer quickly showed that the method of working was a very wasteful one, the graph being practically a uniformly rising line from atmospheric temperature to a maximum of 350° C. (see Fig. 1) at which point (a matter of 16 hours), the gas was

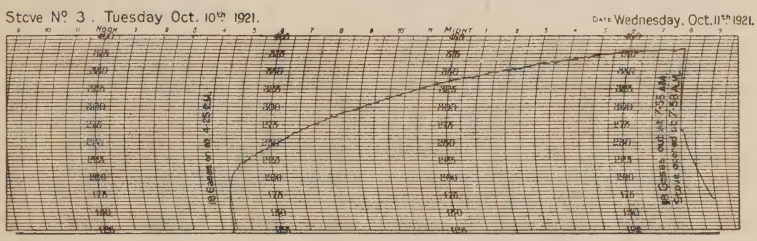


Fig. 1.

No. 3 Mould-drying Stove, fitted with Bunsen Burners, using Town's Gas. Consumption: 25000 cu. ft. Time: 15 hours.

shut off and the moulds withdrawn. This, I think you will agree, is a somewhat extravagant use of heat. A further point noticed was that, in spite of the very high temperature attained, 385° C., quite a number of the moulds were reported to be insufficiently dried, whilst others were burnt. Careful observation showed that the underdried moulds were always found on the bottom layer of the carriage and particularly so at the door end.

A portable recording thermometer was put into service, with the result that the inside of the stove was found to have a decided temperature gradient varying from 385°C. at the roof to 100°C.

at the top of the carriage or floor line of the stoves.

The logic of this was, undoubtedly, to average these conditions as much as possible, more especially as in loading the carriage, large moulds, which, of course, required more drying, were placed at the bottom and small moulds at the top, or, in other words, the moulds were arranged in a reverse order to the temperature gradient within the drying chamber.

Whilst these experiments were in progress, an investigation was carried out in the research laboratory to determine the temperature at which the natural bond of the sand would be broken down, and also the limit of temperature advisable when drying an oil sand core, and the results showed very clearly the importance of drying at a lower temperature than hitherto in use. Consequently, further endeavours were made to reduce the temperature gradient. But before proceeding to describe how this object was attained, it would perhaps be as well to enumerate generally the conclusions arrived at as a consequence of the observations made of the stoves fitted with bunsen burners.

(1) The nature of the flame, either a true bunsen flame or any other form of non- or semi-luminous flame, made no appreciable difference either to the gas consumption or the temperature attained.

(2) The gas pressure was found to be an important factor in the consumption, a slight increase of pressure recording an increased consumption of gas entirely out of proportion to the slight increase of temperature; therefore, steps were taken to regulate the pressure, which was done by putting into circuit a Bryan Donkin Regulator.

(3) Any difference between burners arranged either at one end or down two sides of a stove was so slight as to be incapable of evaluation.

(4) Repeated experiments demonstrated that, whatever the temperature of the stove, a thermometer buried in a core or mould registered no more than 100°C.

(5) Very considerable condensation took place within the stove itself, causing rust on the moulding boxes, nails, heads, chills, etx.; this effect was traced to the high hydrogen content of the gas.

(6) *Insulation.* As an experiment, one of the stoves was insulated by a lining of Moler Bricks, which effected a saving of 2,000 feet of gas per run of 15 hours, and reduced the time required to attain a drying heat; eventually all the stoves were so treated. I consider this a most important matter, deserving close attention whenever furnaces are to be designed.

From the economic point of view, the result of all this was to effect the following saving per stove whenever put into operation:

(i.) 2,250 feet per run by regulation of gas pressure and temperature.

(ii.) 2,000 feet per run by insulation, a combined total of 4,250 feet per run, reducing the consumption from 25,250 feet to 21,000 feet.

This, although a great improvement—and it must not be lost sight of that this saving could be multiplied by 16, the number of stoves in commission—was not considered good enough, and the attack was carried forward on the lines of improving the temperature gradient.

About this time our attention was directed to a gas-fired file-hardening furnace invented by a Sheffield man named Fuller, and it was considered that the burner, which possessed special features, could be adapted to our purpose and, in collaboration with Mr. Fuller, the experiment was made.

The apparatus is of a very simple nature, consisting essentially of a gas and air mixing chamber of special design, Keith Blackman air pressure fan working at 8″ water gauge, and two 4″ steel tubes arranged down each side of the drying chamber and provided with outlets to point towards the centre line of the chamber. In working, gas is passed through the mixing chamber and ignited, the secondary air then being turned on, the effect being to project a flame down the entire length of pipe, some 20′-0″. Next to the mixing chamber a short fireclay sleeve is inserted in the pipe as a protection, the flame at this point being very intense. This installation was started up on 26th June, 1922, and has since operated 6 days per week, the gas consumption averaging 1,000 feet per hour.

Some little time was required to get this apparatus into working order. After acquiring the proper technique, no further trouble has arisen, and, compared with the Bunsen burners, the results have been very satisfactory, the operating time has been reduced by one hour and the gas consumption by over 5,000 feet per run. The cost of working the fan is 1/- per run and nothing has been expended in repairs, except a small sum for renewing the fan impeller.

This installation has the very great advantage of very materially reducing the temperature gradient within the drying chamber and lowering the maximum roof temperature from 385°C. to 225°C. See chart fig. 2.

A further pressure gas installation was tried, made by the British Furnaces Ltd. This is very similar to the Fuller system, the essential difference being that a higher air pressure is employed, and that a much higher temperature is attained at the point of combustion ; the results are very similar, and there is but little difference between the two installations. Although we had had very considerable success with these gas installations we hesitated to proceed further, because it was realized that hydrogen gas was not altogether a suitable fuel for the purpose. As previously

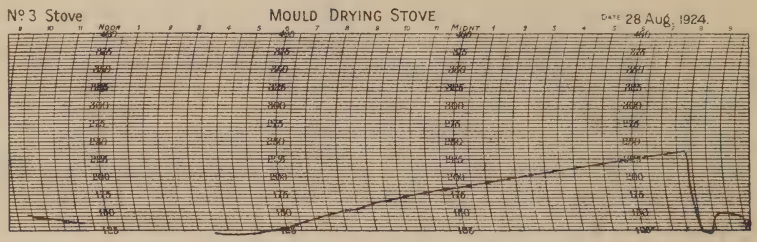


Fig. 2.
No. 3 Stove, fitted with Fullers Burners, using Town's Gas.
Consumption: 15460 cu. ft. Time: 15 hours.

mentioned, considerable condensation was taking place within the drying stove at all temperatures up to boiling point, and this was considered to be an adverse factor from the moulders' point of view.

Many drying problems present themselves for solution in a Steel Works and amongst others is the drying of clay crucible pots used for the production of special alloy steels. This is a very particular operation and the conventional way is to employ a coke furnace and to construct the drying chamber over the flue from the furnace to chimney. This process is wasteful in fuel, and has the further disadvantage of creating a considerable temperature gradient in the drying chamber. This crude method of drying results in a large percentage of wasters, and with this in view and to effect if possible, an economy in the use of coke, other methods were considered, and eventually a high pressure hot water or Perkin's system was installed with complete success; the coke consumption was halved, wasters were practically eliminated and so successful did this installation prove, that a drying stove for cores was fitted up in the foundry. This, however, was a qualified success only, for just about this time we went in extensively for oil sand cores; and this drying system was unable to cope with cores of this nature and had to be abandoned. The reasons were twofold:—(1) The temperature possible in the drying stove was not in excess of 110° C. and (2) it is necessary that oil sand cores should be stoved at a temperature of not less than 180°C. in order that the volatile constituents of the oil be driven off. It should be mentioned that the stove was quite successful in drying plain sand cores.

As a consequence of this experiment and the close observations made of the gas-fired drying stoves, it was recognised that the ideal stove would be one in which the drying medium would be hot gases, or air in as dry a state as possible, and, if possible of attainment, the temperature should be constant. It was also noted that ventilation of the drying chamber was a most important factor and unless intelligently managed would cause very considerable trouble and loss.

It must not be lost sight of that it had been found possible to dry cores at the low temperature of 110°C., and further, the cores thus dried showed a superiority in many respects over those dried at a higher temperature in the gas-fired stoves; this superiority was credited to the lower moisture content of the dry air as against the products of combustion in the gas-fired stoves.

As no doubt you are aware, it is a costly matter to heat up large quantities of air and, although it was desirable that hot air should be employed, this line of investigation was reluctantly abandoned.

Just about this time a coke-fired furnace for mould drying was introduced to our notice by Mr. Arthur Ryner. The claims made for this furnace were so remarkable, that I was instructed to proceed to Germany to make enquiries and, if possible, to see the furnace in operation. This was done, and, as a result, a furnace was ordered and after considerable delay arrived in Sheffield.

It is proper to mention here that this furnace, which is patented throughout the world by Messrs. Hüttenes & Oehm, of Düsseldorf, was applied, where seen in Germany, to drying large moulds in situ, the *modus operandi* being to close the mould temporarily, instal the furnace above, and pass the hot products of combustion into the cavity of the mould, vents being provided at the casting.

The furnace or heating unit itself is simply a steel plate box lined with firebricks, provided with a combustion chamber with firebars and feeding door at top; the fuel used is low grade coke, breeze, lignite, or any other cheap fuel; the hot gases pass over a bridge at one end of the furnace, down each side of vanes or louvres of firebrick between which they are met by a compressed air jet at 80 lbs. pressure per square inch. The effect of this is to increase materially the draught through the firebars, and what is even more important, project the products of combustion into the drying chamber at a high velocity.

Immediately the furnace arrived at our works, it was tried upon a large mould just completed in the foundry floor, with the unfortunate result of burning it up; in fact, spoiling it completely. This was somewhat negative, but at any rate it did show that very considerable temperatures were attained, and gave rise to the suggestion that the furnace should be attached to one of our drying chambers, which was carried out at once and a trial run made with most satisfactory results.

Since this, considerable progress has been made in the adaptation of the furnace to the requirements of mould and core drying in chambers; we make no use of the apparatus at present as a portable appliance for drying moulds in situ, but this will receive attention at a later stage.

As a sequel to our experimental work with the imported furnace, we now construct a brick furnace which, for convenience of operation, is in most cases sunk into the ground. The essential features

of the compressed air jet, firebrick louvres, etc., are retained, but the direction of the hot gases is reversed from a downward to an upward direction. A further development is to operate a number of drying chambers from one furnace only, which is achieved by the employment of as many compressed air jets as drying chambers; we also pre-heat the compressed air very considerably.

These arrangements have proved very economical, which no doubt is to be accounted for, amongst other reasons, by the fact that thermal losses in the furnace are decreased proportionately to the number of drying chambers served.

A further interesting feature is the possibility of carrying the hot gases considerable distances at high velocity and with little loss of heat; the farthest point to which we have at present carried the gases from the furnace to the drying chambers is 32 feet.

To sum up, the advantages to be attributed to this type of furnace, used for the purpose described, may be enumerated as follows:—

(1) The fuel consumption is economical.
(2) It requires little attention during the run.
(3) Within the limits of the apparatus the temperature may be readily regulated without difficulty by turning on more or less air.
(4) It takes up very little space and is quite cheap to build and maintain.
(5) It does not require a chimney.
(6) It can, if necessary, be placed at some distance from the drying chamber with little loss of thermal units.
(7) One furnace may be used to serve a number of drying chambers, thereby reducing labour at the furnace and cheapening the construction.
(8) A satisfactory thermographical chart may be closely copied, thus providing an invaluable guide to the operator. See chart fig. 4.
(9) The cheapest available fuel above the grade of dust may be used. We are using cinders obtained from the Corporation cleansing department collected with the household refuse.
(10) Whenever compressed air is in use, it provides a useful night load and so reduces the overhead charges on this item of plant.
(11) The air consumption is low and the charges therefor small.
(12) The hot gases may, with facility, be conducted to any part of the drying chamber and, together with the ventilation, dispositions may be made to produce either an equable temperature throughout the chamber or any desired temperature gradient within the capacity of the installation.

(13) Complete combustion is attained ; only slight traces of CO have been shown whenever analyses were taken.

(14) The drying chambers are under pressure with considerable circulation currents in the hot gas.

(15) Ordinary unskilled labour may be employed to operate the installation, a thermograph chart being a record of all that takes place during a run, and at the same time a guide to the operator.

Very careful observations have been made of the performance of these furnaces for the past 10 months, and although by no means complete, the data so obtained are, I venture to say, sufficient to substantiate all the claims just made, and it will now be my duty and pleasure to put this information before you.

The furnace upon which the tests were made is arranged at one end of a large drying chamber for moulds. The drying chamber is 24′-6″ long, 11′-0″ wide and 8′-0″ high, with a cubic capacity of 2,156 c.ft. The moulds are conveyed into the chamber by means of a travelling carriage, which is sealed by a sand trough, the floor of the carriage being constructed of iron plates insulated by asbestos millboard. The walls of the drying chamber are 14″ thick in red brickwork, and the roof construction is of steel joists, between which are sprung small jack arches of two half brick rings, the outside of the roof being covered with "Moler" insulation bricks. The door is balanced and made to lift vertically and constructed of steel plates, between which asbestos is sandwiched.

The furnace, which is quite small, is situated at the end opposite the door, is constructed of 4½″ best quality firebrick surrounded by "Moler" insulating bricks, the outside being 4½″ red brickwork. The furnace is sunk into the ground, the top being at ground level.

The products of combustion are carried into the drying stove by a brick flue and inside the stove carried forward and equally distributed by a 10″ cast iron perforated pipe supported on, and situated down the longitudinal axis of the carriage in such a way as to register with the brick flue from the furnace.

This device is quite simple and effective and is adopted as a standard, but in some instances, the distributing pipe is carried either down one side or across one end of the drying chamber as found most convenient, it being understood that in every case the layout is designed to suit existing arrangements.

The moulds in their cast iron boxes are piled up on the carriage, small spaces being arranged around, above and below each box to permit the hot gases to circulate. No particular order is observed in the packing, but generally speaking, for convenience of handling, the large boxes are placed at the bottom and the small boxes at the top of the pile. Every endeavour is made to place as many moulds as possible upon the carriage. An average load would be 30 to 35 tons including cast iron boxes and sand.

Such is the efficiency of the apparatus that all the moulds are thoroughly dried at the end of the run and no moulds are found to be burnt or imperfectly dried. As in some cases the thickness of rammed sand to be dried is up to 15″, contained in a cast iron box $\frac{7}{8}$″ to 1″ thick, a period of 15 hours only for drying may be considered rapid.

To return to the furnace itself.

The grate area is 7 square feet, the firebars being of cast iron, of similar design to those in common use in a Lancashire Boiler. The outlet flue conveying the hot gases into the drying chamber is 10″ diameter, the compressed air jet being $\frac{3}{16}$″ diameter and the air pressure 80 lbs.

In lighting the furnace a bed of coke is placed upon the bars, a few shovelsful of burning coke or cinders placed on top and the air turned partially on. In about 20 minutes the furnace is well alight, the air is then turned fully on, the furnace fed from time to time with fresh fuel and the firebars kept clean. The time temperature chart shows clearly the time at which these operations are performed during a run.

The average working temperature employed for mould drying is 225°C., for large cores 200°C. and for small cores 180°C. See charts figs. 3 and 4.

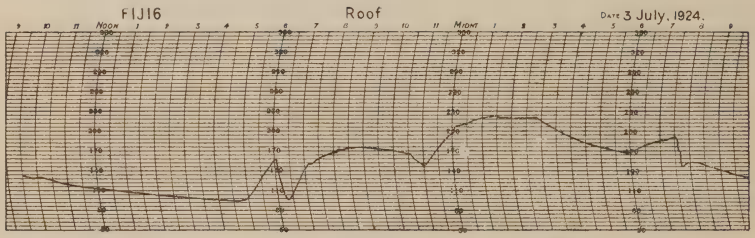


Fig. 3.
No. 16 Mould-drying Stove, fitted with New Coke Furnace.

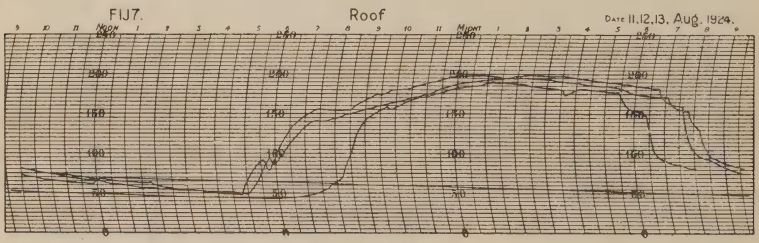


Fig. 4.
No. 7 Mould-drying Stove, fitted with New Coke Furnace showing three separate days run.
TYPICAL THERMOGRAPHS.

The fuel burnt is as follows :—

Mould Drying Stoves ..	7 cwts.	of coke	per run	of 15	hours.		
Large Core ,, ..	$4\frac{1}{2}$	,,	,,	,,	,,	,,	
Small Core ,, ..	4	,,	,,	,,	,,	,,	

I am unable to give you the air consumption in terms of cubic feet per minute, but tests have been taken of the electrical units consumed, which were found to be as follows :—

The air is supplied by the foundry air compressor plant, which consists of two Belliss & Morcom high speed two stage compressors, electrically driven, of 150 cubic feet free air capacity. They are fitted with electrical meters and it is quite easy to ascertain the amount of current consumed.

During a period of six hours operating one furnace only, the electrical energy consumed was found to be 52 units. The air service being extensive, and the stove under test at the end of the pipe being farthest from the compressor, it is necessary to make a correction for leaks, and other loss of efficiency. Therefore, a further run of 6 hours was made with all air using units cut out of service, and it was found that 30 electrical units were expended ; deducting this amount from the gross total previously given, we have 22 as the nett amount of current consumed in a run of 6 hours or at the rate of 3·6 per hour, the nett cost for current only being $1/7\frac{1}{2}$d. per run of 6 hours.

A further test was made with 5 jets in operation and the consumption in this case was found to be 189 units. Making the same deduction, viz. : 30 units, the nett amount of current consumed in a run of 6 hours using 5 jets is 159 units, or an average of 32 units per jet per 6 hours.

The fuel consumption is low, as the following table will disclose

No. 1 Furnace,	average per hour	for 1 month	..	32 lbs.
No. 2	do.	do.	..	56 ,,
No. 3	do.	do.	..	36 ,,
No. 4	do.	do.	..	36 ,,

In conclusion, it would, I think, be of interest to read to you the results of a test made on No. 2 furnace as recently as 18th August, 1924.

Test made on August 18th, 1924. *Burning Coke Breeze.*

Average temperature in drying chamber 190°C., in the centre of the chamber at a point 6″ from the underside of the roof ; practically the same reading was obtained at the end next the furnace at a point midway between the carriage floor and the underside of the roof.

A further reading was taken on top of the carriage next to the outer door which gave an average of 150°C. The temperature of the products of combustion at a point between the louvres and immediately inside the drying chamber ranged from 920°C. to 740°C. over a period of two hours. See chart fig. 5.

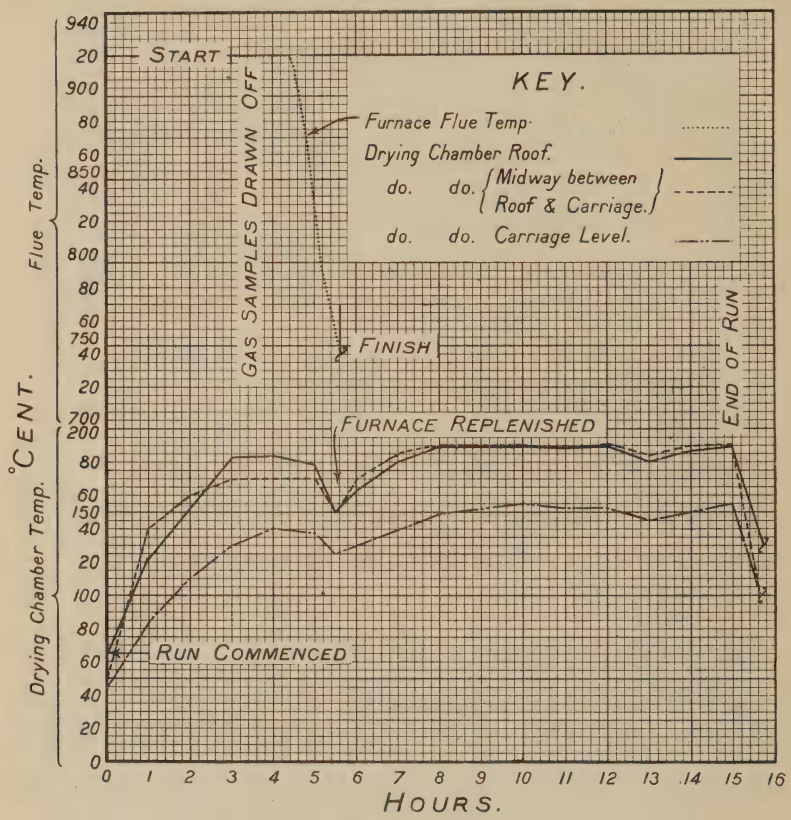


Fig. 5.
Graph showing Temperatures in Flue and Drying Chamber, fitted with Air-blown, Coke-fired Mould-Drying Apparatus.

Air pressure was maintained at 80 lbs. as shown on thegauge. This pressure was shown by previous experiments to be the most efficient.

The ventilation outlets were set to give a total of 48 sq. inches area, also determined by previous experiment.

This is, of course, in addition to leakages through door jambs, etc.

Samples of the products of combustion were taken both when just leaving the furnace and after admixture with the compressed air and analyzed, the samples being drawn off simultaneously, the temperature in the flue pipe being 920°C. The results of this analysis are as follows :—

Before admixture with Compressed Air	*After* admixture with Compressed Air
CO_2 = 13·15%	CO_2 = 13·96%
O_2 = Nil.	O_2 = 5·23%
CO = 12·85%	CO = 0·41%

II.—The Action of Heat on Kaolinite and on Kaolinitic Clays.

By W. Vernadsky.

In a recent paper by J. W. Mellor and A. Scott[1] on the action of heat on kaolinite and other clays, the authors put forward their explanation of the known facts relating to this very complicated phemomenon.

However, in the present state of our knowledge, these facts appear to me to suggest a different interpretation ; and it is the object of this short paper to outline this alternative explanation. Only by testing the validity of these new representations by new experiments and observations can we elaborate a theory of this very important phenomenon. This theory presents not only a scientific, but also a practical interest.

It seems to me that the behaviour of kaolinite in the thermic field of our experiments (0-2000°C.) indicates that *all observed transformations correspond to one and the same process.*

These changes are in close agreement with the chemical structure and the chemical functions of kaolinite and kaolinitic clays[2]. The process of decomposition of kaolinite consists in gradual loss of water and silica and in a corresponding chemical transformation of the alumosilicic residue. *We observe a gradual transformation of the complex alumosilicic acid—*$Al_2Si_2O_6(HO)_2 \cdot H_2O$ *(kaolinite)—into a definite alumosilicic anhydride, the formula of which is* $Al_6Si_2O_{13}$ *or* $Al_8Si_3O_{18}$ *(mullite or keramite).*

I. DEHYDRATION OF KAOLINITE.

The process begins by dehydration of kaolinite, *i.e.*, by the formation of a complex alumosilicic anhydride from an alumosilicic hydrate.

From a chemical point of view, kaolinite and kaolinitic clays may be considered as *alumosilicic acids* of peculiar chemical constitution. The different chemical character of molecules of water in kaolinite is proved beyond doubt[3]. In kaolinite—$2H_2OAl_2O_32SiO_2$—*only one molecule of water can be replaced by bases.* Thousands of cases of this reaction are observed in the earth's crust and in the laboratory. Furthermore, no difficulty is experienced in obtaining many different anhydrous or hydrated salts of kaolinitic acid, such as $Na_2Al_2Si_2O_8$, $K_2Al_2Si_2O_8$, $CaAl_2Si_2O_8$, $Na_2Al_2Si_2O_8$ $4H_2O$, etc., from kaolinite and kaolinitic clays, or in producing the contrary reaction, viz., converting these salts into kaolinite or kaolinitic clays. If the character of but one molecule of water is clear, the chemical nature of the other can be expressed hypothetically as one of *zeolitic water.*

The formula of kaolinite, $2H_2OAl_2O_32SiO_2$, may then be written:

$$Al_2Si_2O_6(HO)_2 \cdot H_2O.$$

Our actual knowledge of the properties of zeolitic water is, generally speaking, very incomplete. It is a form of dissolved water, *a case of solid solution,* but a very peculiar one. It is a solution in the crystalline space lattices. The forces which come into play in the phenomenon of the zeolitic solutions are of a crystalline, vectorial nature. The simple molecular relations between the zeolitically dissolved substance (water in this case) and the crystalline space-lattices ($Al_2Si_2O_6(HO)_2$ in this case) are manifestations of regularity of structure of the crystalline field of crystalline lattices. They correspond only to a complete equilibrium and can exist as such only in a definite thermodynamic field. At other temperatures the zeolitic solution is in a state of dissociation; zeolitic parts can enter and disappear without altering, or very little, the crystalline structure (crystalline lattices), which is determined by the properties of the solvent.

There are some vague analogies between colloidal and zeolitic water; but the differences are greater. Colloidal water is retained by superficial forces of crystalline particles (micels), the zeolitic water by interior forces of crystals (space lattices). In the first case the vectorial properties of the matter are invisible; in the other they determine the phenomenon.

In the phenomenon of heating, the twofold character of the water of kaolinite is not very apparent under the ordinary conditions of our experiments. There must be some explanation of this fact, but it cannot yet be stated with absolute certainty.

But, in explaining the phenomenon of heating, the twofold character of the water of kaolinite, which is proved by chemical observations and experiments, must not be overlooked.

It is evident that the twofold character of the water must, in one way or another, be expressed in the phenomenon of heating. If it is not clearly manifested, it must be complicated by secondary phenomena, probably due to the properties of zeolitic water.

But it is clearly expressed in the *different thermal effects* which accompany the loss of the two types of water. A great part of the water is lost at a definite temperature (450-460°C.), and is accompanied by *absorption of heat,* as was established by Le Châtelier. The other portion of the water disappears on heating proportionately to the rise of temperature *without any expressed thermal effect.* It seems that the quantity of water, the loss of which is accompanied by latent heat, corresponds to one molecule (about 7 per cent. by weight—*e.g.*, in the experiments of Prof. J. Samoilov, 1912, Prof. V. Agafonoff in 1924, etc).

The manifestation of a thermal effect is characteristic of a chemical process and must correspond to the destruction of the compound $Al_2Si_2O_6(HO)_2$, which forms the space-lattices of the

kaolinite. Above the temperature point of latent heat the crystalline structure of the compound (solvent) is changed and kaolinite, as such, ceases to exist. As is shown by experiments, the kaolinite is transformed into an anhydrous leverrierite—$Al_2Si_2O_7$.[4].

But the dehydration begins before this temperature point is reached. This loss of water does not manifest itself in thermal curves. The beginning of this dehydration is not associated with one fixed temperature point, but varies for different specimens of kaolinite and under varying experimental conditions. Apparently, in crystalline kaolinite (*i.e.*, when crystal individualities can be seen under the microscope), this water begins to disappear at temperatures above 100°C. At this moment kaolinite presents all the properties of a substance in a state of dissociation. We must conceive this water as dissociated from zeolitic solution. The zeolitic water begins to disappear *before* the chemically bound water, but this loss is not terminated at the point of decomposition of alumosilicic hydrate and is interrupted by the heat absorption associated with the chemical transformation of a crystalline compound (formation of leverrierite) and with a constant temperature (latent heat).

When this chemical transformation is complete, the temperature begins to rise and zeolitic water again begins to dissappear. The last traces of zeolitic water in crystalline lattices can be expelled only with great difficulty at high temperatures.

The process of dehydration can be represented by the following table :—

At Ordinary Temperatures.	Kaolinite.	$Al_2Si_2O_6(HO)_2.H_2O$.
	↓	↓
>100°–450°C.	Kaolinite in a state of dissociation.	$Al_2Si_2O_6(HO)_2(1-q)H_2O+qH_2O$.
	↓	
450°–460°C.	Hydrated leverrierite in a state of dissociation.	$Al_2Si_2O_7(1-q)H_2O+qH_2O$.
	↓	
<600°C.	Anhydrous leverrierite.	$Al_2Si_2O_7$.

The temperature 450-460°C.—a definite range of temperature—must divide the *kaolinitic field* from the *leverrierite field.* Both these compounds can contain zeolitic water.

NATURE OF DECOMPOSITION OF KAOLINITE AT 450—460°C.

The existence of anhydrous leverrierite above 460°C. is, it seems to me, established by experiments the results of which have recently been published[5]. Above this temperature the dehydrated kaolinite is homogenous and crystalline ; no amorphous or vitreous substance exists. The anhydrous leverrierite here obtained has definite optical properties which differ from those of kaolinite and a different specific gravity. The determination of the density of the dehydrated

product is alone sufficient to verify the hypothesis of the decomposition of dehydrated kaolinite into free silica and free alumina.

Calculation shows that a mixture of one molecule of Al_2O_3 and two molecules of SiO_2 (cristobalite) must have a density of 3·08; we found the density to be 2·32–2·38, while according to G. Tammann and W. Pope[6] it is 2·50–2·56. This low density of the dehydration product is incompatible with the hypothesis of the formation of a mixture of $Al_2O_3+2SiO_2$.

It is important to note that this hypothetical decomposition of $Al_2Si_2O_7$ is contradictory to all our knowledge of the chemistry of alumosilicates and of the history of natural alumosilicic minerals. We have here a very solid complex of facts which must be taken into consideration. Every explanation of observed phenomena, which is not in agreement with these well established chemical and mineralogical data, must be rejected.

It is firmly established that the complex $Al_2Si_2O_7$ is a very stable one in natural and artificial compounds. It does not change in thousands of chemical reactions and remains unchanged in many transformations of alumosilicates. In the earth's crust the kaolinites and kaolinitic clays are always produced by the transformation of peculiar alumosilicates (felspars and others), which contain this characteristic complex of elements. This complex of kaolinite is never formed from free silica (or silicates) and free alumina (aluminates). The kaolinite and kaolinitic clays are generally transformed by metamorphism into the same alumosilicates, which contain the complex $Al_2Si_2O_7$.

This complex is formed from free silica (or silicates) and free alumina (or aluminates) only at high temperatures in the magmas or, at high pressures, in hydrothermal reactions above 180°C. We have not succeeded in obtaining it in the laboratory under other thermodynamical conditions. It seems that the formation of $Al_2Si_2O_7$ is an endothermic process.

The compound $Al_2Si_2O_7$, in a free state, has the properties of an anhydride; with water it forms acids, with metallic oxides, salts.

The bond between Al_2O_3 and SiO_2 can only be destroyed by the action of strong acids. At high temperatures the salts of $Al_2Si_2O_7$ are stable (up to 1,800°C.); free $Al_2Si_2O_7$ does not exist above 1,000°C only.

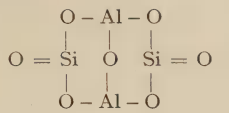
The hypothetical decomposition of $Al_2Si_2O_7$ at a temperature of 450–500°C. has no analogy in known phenomena occurring in the earth's crust or in the laboratory.

The facts enunciated in the preceding paragraph may be generalised in an empirical representation on the hypothesis that the complex $Al_2Si_2O_7$ forms, in compounds in which it exists, a peculiarly stable nucleus, a complex of elements which has a real, independent existence.

Its stability under many different reactions can be expressed

by a cyclical structure, analogous to other cyclical structures known in natural compounds (benzols, naphthenes).

The simplest representation of this *kaolinitic nucleus* would then be :

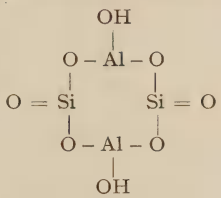


anhydrous leverrierite.

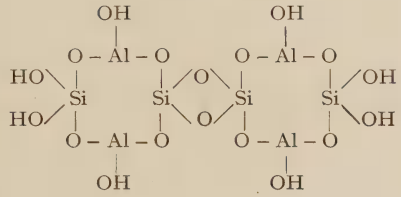
We must admit, in order to explain the known facts of the chemistry of alumosilicates, (1) that hydroxyl groups are bound with Al atoms and (2) that a few kaolinitic nuclei can be bound together.

We then obtain the following formula :—

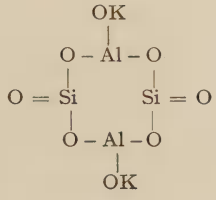
Kaolinitic acid (not known)



Kaolinite.



Phacellite



III. NATURE OF TRANSFORMATION AT 900–1060°C.

Many years ago, H. Le Chatelier showed, for the first time, that there is a very obvious *escape of heat* at about 900-1,000°C. during the heating of kaolinite.

This heat liberation is often explained by a polymorphic transformation of free Al_2O_3. We have seen that the existence of free Al_2O_3 in dehydrated kaolinite is very doubtful and contradicts the homogeneity of this substance. The temperatures of liberation of heat, of polymorphic transformation of alumina and of the heating

of kaolinite do not correspond. The polymorphic transformation of alumina takes place between 800–900°C., while the heat liberation of kaolinite occurs at 900–1,000°C.[8].

The heat liberation receives a simple explanation in admitting the existence of anhydritic leverrierite in dehydrated kaolinite.

Leverrierite does not exist at high temperatures. It is never found in the corresponding conditions of the earth's crust and is decomposed on heating. This decomposition is *accompanied by heat liberation, because leverrierite—$Al_2Si_2O_7$—and kaolinitic nuclei generally, are endothermic compounds.* This temperature represents the limit of the leverrierite field. Above it leverrierite cannot exist.

FORMATION OF SILLIMANITE.

The nature of the product formed by its decomposition under these conditions has not been definitely determined. It seems, from recent experiments of N. Bowen and J. Grieg[9], that the process of the decomposition of $Al_2Si_2O_7$ is accompanied, not by the formation of *sillimanite*—Al_2SiO_5—, but of an alumosilicic anhydride, richer in alumina—*mullite*[10], or *keramite*[11]. It is certain that, by this decomposition, free silica (cristobalite according to N. Bowen and J. Grieg) is liberated, but in *many cases* the reaction does not correspond to the equation:

$$\underset{\text{anhyd.leverrier.}}{Al_2Si_2O_7} = \underset{\text{sillimanite.}}{Al_2SiO_5} + \underset{\text{cristob.}}{SiO_2}$$

It corresponds to the equation:

$$\underset{\text{anh. leverr.}}{3Al_2Si_2O_7} = \underset{\text{mullite}}{Al_6Si_2O_{13}} + \underset{\text{crist.}}{4SiO_2} \quad \text{or}$$

$$\underset{\text{anh. leverr.}}{4Al_2Si_2O_7} = Al_8Si_3O_{18} + \underset{\text{crist.}}{5SiO_2}$$

N. Bowen and J. Grieg could never obtain sillimanite by heating the kaolinitic clays under different conditions; they always obtained mullite, to which they gave the formula $Al_6Si_2O_{19}$. The published analyses are perhaps better expressed by the formula $Al_8Si_3O_{18}$, which I proposed many years ago[12].

But sillimanite certainly exists in nature, where it is formed under conditions very analogous to those of the laboratory, viz., by the action of heat or great pressure upon kaolinitic clays.

In my former experiments[13] I obtained crystals which could be analysed and gave the formula of Al_2SiO_5 (sillimanite). In two determinations of SiO_2, I obtained 36·8–37·31 per cent., and for Al_2O_3–63·65 per cent. Other experiments gave me a product, which could not be microscopically distinguished from sillimanite, but the analyses gave 28·6–29·5 per cent. SiO_2[14]. It is mullite or keramite.

I could not determine the conditions at which sillimanite was formed. It seemed to me that it was formed near the temperature

of heat liberation[15]. The addition of 1—2 per cent. MgO appeared to favour the formation of sillimanite[16].

FORMATION OF MULLITE (KERAMITE).

As a rule it is not sillimanite, but a product richer in Al_2O_3—*mullite or keramite*—which is formed under these conditions.

The recent experiments by American chemists confirm my early results and deductions. My work was published in Russia as a thesis at the University of Moscow and was reprinted (with a French resumé) in *Bulletin de la Société des Naturalistes de Moscou.*[17] I now find that specialists are unacquainted with this work.

In 1891, the action of heat on kaolinite was represented by me by the following scheme[18].

$$\begin{array}{lcl} Al_8Si_8O_{28}. & & \\ \downarrow & & \\ Al_8Si_4O_{20} & - & \text{sillimanite.} \\ \downarrow & & \\ Al_8Si_3O_{18} & & \\ \downarrow & & \\ Al_8O_{12} & - & \text{corundum.} \end{array}$$

This scheme is very similar to that of N. Bowen and J. Grieg. The differences are to be found in admitting the existence of the sillimanite field and in the formula for mullite, which I gave as $4Al_2O_3 3SiO_2$ and not $3Al_2O_3 2SiO_2$.

It has hitherto been very difficult to decide which of the formulæ—$Al_8Si_3O_{18}$ or $Al_6Si_2O_{13}$—best expresses the composition of mullite. In 1891 I indicated that it was impossible for me to distinguish the different varieties of rhombic alumosilicic anhydrides by optical methods[19]. Now, despite the great progress in our optical methods and the splendid equipment of the Carnegie Laboratory, the American savants have come practically to the same conclusion[20]. The rhombic varieties cannot be distinguished one from the other by ordinary optical methods.

We must, therefore, turn to chemical analysis. It follows from the table, that these analyses do not enable us to decide which formula—$Al_6Si_2O_{13}$ or $Al_8Si_3O_{18}$—is the better. Do both compounds exist? Further investigations alone can decide.

TABLE OF ANALYSES OF MULLITE.

		$Al_6Si_2O_{13}$.	$Al_8Si_3O_{18}$.	Ste.Cl.Deville	Vernadsky.
SiO_2	..	28·2	30·6	29·1–29·5	29·7
Al_2O_3	..	71·8	69·4	70·2–70·9	70·3

		Vernadsky.	Vernadsky (Kaolinite)	Littleton.	Bowen.
SiO_2	..	29·8–30·7	29·9–30·1	27·35–27·60	29·36
Al_2O_3	..	—	—	72·87–73·16	69·05

		Zies.	Cox.	Cox.
SiO_2	..	29·04	30·07	28·89
Al_2O_3	..	69·63	69·93	71·11

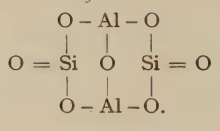
The existence of a few different alumosilicic anhydrides rich in Al_2O_3 is very probable. Some groups of alumosilicates, such as dumortierite or grandidierite, cannot be explained otherwise.

In the present state of our knowledge we can represent the whole process of heating kaolinite by the following scheme :—

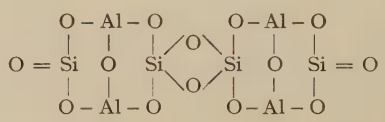
1. *Kaolinitic Field.* 0 – 450°C.
   $Al_2Si_2O_6(HO)_2.H_2O$
   ↓
   $Al_2Si_2O_6(HO)_2.(1-q)H_2O+qH_2O.$
   ↓
2. *Leverrierite Field.* 450–1,060°C.
   $Al_2Si_2O_7.(1-q)H_2O+qH_2O.$
   ↓
   $Al_2Si_2O_7.$
   ↓
3. *Sillimanite Field.* ? 1,000°C. – ?
   $Al_2SiO_5+SiO_2.$
   ↓
4. *Mullite Field.* 1,200 – 1,800°C.
   $Al_8Si_3O_{18}+SiO_2$
   ↓
   $Al_6Si_2O_{13}+SiO_2$
   ↓
5. *Corundum Field.* 1,800 – 1,920°C.
   Al_2O_3+liquid.

It is interesting to note that very simple structural representations of these compounds—in agreement with many of their chemical properties—can easily be constructed, *e.g.*:—

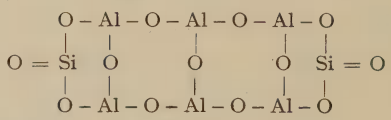
Leverrierite.



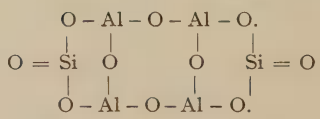
or



Mullite
(N. Bowen and J. Grieg.)



Sillimanite.



The formula of N. Bowen and J. Grieg for mullite, viz., $Al_6Si_2O_{13}$, is more simple and corresponds more nearly to the theory of kaolinitic nuclei than $Al_8Si_3O_{18}$.

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7. By biochemical processes $Al_2Si_2O_7$ is decomposed at low temperature, *cf.* W. Vernadsky, *La géochimie.* 1924, p. 174.
8. The determinations of G. Tammann and W. Pope give 850° and 1,060° for pure free alumina and 930° for kaolinitic Oschatz clay. (*l.c.* 1923, 49).
9. N. Bowen and T. Grieg, *J. Amer. Cer. Soc.*, **7**, 238, 1924.
10. N. Bowen, T. Grieg and E. Zies, *J. Wash. Acad. Sc.* **14**, 183, 1924.
11. J. W. Mellor and A. Scott, *l.c.*, 1924.
12. W. Vernadsky. *Bull. Soc. Natur. Moscou.* 1891, p. 545.
13. W. Vernadsky, *l.c.*, 1891, p. 74-76.
14. On heating topaz, the homogeneous cristalline residue gave 29·8 – 30·4% SiO_2 (*l.c.*, 1891, p. 78-79).
15. *i.e.* 1,000°C. ; sillimanite seemed to be the first product of the decomposition of $Al_2Si_2O_7$ (*l.c.*, 1897, p. 74).
16. W. Vernadsky, *l.c.*, 1891, p. 76.
17. *l.c.* p. 1-100. French resumé, *ib.*, 1891, p. 165.
18. W. Vernadsky, *l.c.*, 1891, p. 77.
19. W. Vernadsky, *l.c.*, 1891, p. 72, *et seq.*
20. Alumosilicic anhydride, $Al_4Si_3O_{18}$, obtained by Fremy and Feil, must be monoclinic or triclinic (Jeannetaz by Fremy et Feil, *Comptes rend.*, 85. 1877, p. 1,033). On repeating their experiments, I obtained rhombic crystals. (*l.c.*, 1891, p. 70).

DISCUSSION.

Messrs. N. L. Bowen and J. W. Greig—(communicated): Professor Vernadsky's paper is of interest to us principally on account of his discussion of the composition of the crystalline compound, mullite, which forms in alumina-silica mixtures under laboratory conditions. Though he finally accepts our formula, $3Al_2O_3.2SiO_2$, we confess that we derive little satisfaction from his acceptance, based as it is on the questionable evidence of structural formulae and prefaced as it is by a long discussion, the trend of which is towards the conclusion that the composition of the crystals is really $4Al_2O_3.3SiO_2$ as he assumed some years ago. Professor Vernadsky's discussion is calculated to give to the ceramist, who is not also a mineralogist, the impression that there is no way of establishing the composition of mullite or of distinguishing mullite from sillimanite except by chemical analysis. As a matter of fact, analysis is the least trustworthy method of accomplishing these results, because mullite is not ordinarily obtained free from foreign material which in practically all cases is very siliceous. Considering this fact, it is noteworthy that all twelve analyses given by Vernadsky lie on the alumina side, not

the silica side of $4Al_2O_3.3SiO_2$. Even chemical analysis makes it plain, then, that the composition of the crystals is not $4Al_2O_3.3SiO_2$, but is definitely more aluminous.

However, it is not upon analysis, but upon synthesis, that the establishment of the composition of mullite depends primarily. The mixture of alumina and silica in the 3 : 2 proportion is the only mixture which can be converted in the laboratory into a mass consisting entirely of crystals of mullite. Any other mixture gives mullite crystals, to be sure, but they are always accompanied by another phase which represents the excess of alumina or of silica and the 4 : 3 mixture is no exception in this respect.

Chemical analysis is, moreover, by no means the only method of establishing the individuality of sillimanite and of mullite. Optical methods are thoroughly competent to do this and it is quite misleading to state that we "have come practically to the same conclusion" as Vernadsky reached in 1891, viz., "that it was impossible to distinguish the different varieties of rhombic alumo-silicic anhydrides by optical methods." The refractive indices of mullite differ from those of sillimanite by amounts that are from 10 to 15 times the error of measurement of these quantities by methods now available in any progressive mineralogical laboratory. There is no need of the "splendid equipment of the Carnegie Laboratory" nor of the acumen of "the American savants."

We may add, too, that sillimanite and mullite are readily distinguished by their thermal behaviour.

One other remark of Vernadsky's calls for comment, viz.: that in which he states that he differs from us in admitting the existence of a sillimanite field. We are well aware of the occurrence of sillimanite in nature and, in fact, definitely suggested that sillimanite has a field of stable existence at low temperatures (below 1,050°C.). We were, however, constrained to record our failure to prepare it at any temperature. A few investigators, including Vernadsky, believe they have succeeded in preparing sillimanite, but their conclusion is based solely on chemical analysis which, as we have seen, is not dependable. Until some investigator obtains a crystalline product which has the composition of sillimanite and which is proven by microscopic examination to consist entirely of one kind of crystals with the precise optical constants of sillimanite, we believe it is safer to regard the preparation of sillimanite as not yet accomplished.

III.—Alumina-Silica Minerals in Firebricks.

W. J. Rees, B.Sc., (Tech.), F.I.C.

FOLLOWING the publication of the work of Bowen and Greig on the Alumina-Silica system[1], I have examined a number of firebricks of varying composition in order to ascertain the composition of any alumina-silica minerals which had been formed in them during their burning.

Average samples of the bricks were obtained by crushing, and a small portion was ground to an impalpable powder in an agate mortar. One gram of this powder was then added to 20 cc. of pure hydrofluoric acid in a platinum vessel and left for 12 hours. It should be pointed out that the alumina-silica minerals are not insoluble in hydrofluoric acid, complete solution taking place in 3 or 4 days' exposure, so that the results as to the proportions of alumina-silica minerals found in the firebricks examined are only approximate. A uniform time and temperature of exposure to the hydrofluoric acid was adopted so that the results would be comparable.

The following are typical results obtained :—

1. *Firebrick Analysis.*

SiO_2	49·74%
Al_2O_3	43·35%
TiO_2	1·86%
Fe_2O_3	3 21%
CaO	0·62%
MgO	0·66%
Alk. (As K_2O)	0·52%
	99·96%

Brick as received.

Insoluble inHydrofluoric Acid.

14·4%

Composition of Insoluble Residue.

Al_2O_3	72·8%
SiO_2	27·0%
Fe_2O_2	0·2%

Brick reburned at Cone 18 *for* 12 *hours.*

Insoluble in Hydrofluoric Acid.

18·9%

Composition of Insoluble Residue.

Al_2O_3	71·8%
SiO_2	26·6%
Fe_2O_3	1·0%

Brick reburned at Cone 26 *for* 12 *hours.*

Insoluble in Hydrofluoric Acid.

34·4%

Compo8ition of Insoluble Residue.

Al_2O_3	72·1%
SiO_2	26·4%
Fe_2O_3	1·8%

1 *J. Amer. Cer. Soc.*, 7, 238, 1924.

The very considerable increase in the proportion of material insoluble in hydrofluoric acid with increase in temperature of burning is noteworthy. Its composition agrees fairly closely with that of Bowen and Greig's mineral Mullite—$3Al_2O_3 . 2SiO_2$ (Al_2O_3 71·8%, SiO_2 28·2%).

2. *Firebrick Analysis.*

SiO_2	51·89%
Al_2O_3	42·14%
TiO_2	1·48%
Fe_2O_3	3·12%
CaO	0·44%
MgO	0·3[illegible]%
Alk. (As K_2O)	0·62%
	100·08%

	Insoluble in Hydrofluoric Acid.	Composition of Insoluble Residue. Al_2O_3	SiO_2	Fe_2O_3
Bricks as received	22·0%	71·4	26·1	0·9
Reburned at Cone 18	26·8%	70·9	26·0	1·2
Reburned at Cone 26	33·0%	71·8	26·4	2·1

The increase in the proportion of material insoluble in hydrofluoric acid is again noteworthy.

3. *Firebrick Analysis.*

SiO_2	67·16%
Al_2O_3	27·41%
TiO_2	1·04%
Fe_2O_3	1·96%
CaO	0·44%
MgO	0·61%
Alk. (As K_2O)	1·29%
	99·91%

	Insoluble in Hydrofluoric Acid.	Composition of Insoluble Residue. Al_2O_3	SiO_2	Fe_2O_3
Brick as received	8·9%	72·9	26·9	0·6
Reburned at Cone 18	11·2%	72·0	26·4	0·8
Reburned at Cone 26	13·1%	71·7	25·9	1·2

It is to be noted that, with this more siliceous brick, a much smaller proportion of material insoluble in hydrofluoric acid is obtained, but its composition still agrees fairly well with that of the mineral mullite, $3A1_2O_3 . 2SiO_2$.

4. *Firebrick Analysis.*

SiO_2	49·11%
Al_2O_3	43·98%
TiO_2	4·08%
Fe_2O_3	1·88%
CaO	0·21%
MgO	0·24%
Alk. (as K_2O)	0·54%
	100·04%

	Insoluble in Hydrofluoric Acid.	Composition of Insoluble Residue.		
		Al_2O_3	SiO_2	Fe_2O_3
Brick as received ..	14·8%	69·7	29·4	0·7
Reburned at Cone 18 ..	22·4%	69·3	29·2	0·9
Reburned at Cone 26 ..	32·6%	69·5	29·4	0·9
Reburned at Cone 32 ..	42·4%	74·4	24·4	1·4

The rate of increase of formation of the mineral insoluble in hydrofluoric acid is much the same as with the other aluminous bricks examined, and its composition again agrees with $3Al_2O_3 . 2SiO_2$, except in the case of the sample reburned at Cone 32. A portion of this sample was exposed to hydrofluoric acid for 72 hours; the residue was 4·2% and consisted of alumina only. It would appear from this that at the high temperature of firing, some corundum has been formed. It appeared possible that this alumina might be due to hydrolysis of aluminium fluoride; consequently, further observations of the behaviour of these solutions was made, but in no case, from a solution of the strength worked with, was a precipitation of more than 0.003 gram Al_2O_3 obtained in 72 hours. A similar result was obtained on reburning another aluminous brick at Cone 32.

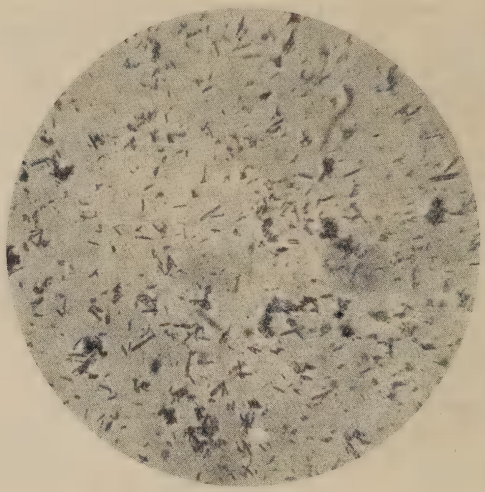
5. *Firebrick Analysis.*

SiO_2	56·26%
Al_2O_3	36·84%
Fe_2O_3	2·19%
TiO_2	1·31%
CaO	0·52%
MgO	0·96%
Alk. (as K_2O)	1·98%
	100·06%

	Insoluble in Hydrofluoric Acid.	Composition of Insoluble Residue.		
		Al_2O_3	SiO_2	Fe_2O_3
Brick as received ..	8·4%	66·9%	32·1	0·2
Brick reburned at Cone 18	16·2%	71·4	28·8	0·4
Brick reburned at Cone 26	27·2	72·7	27·8	0·5

This brick is richer in fluxes than other aluminous bricks examined, and the residue in the brick as commercially burned approximates more to the composition $4Al_2O_3 . 3SiO_2$, but on burning at higher temperatures the composition of the residue changes and again approximates to $3Al_2O_3 . 2SiO_2$.

In all cases the residues contain iron oxide, and this would appear to be in solid solution in the mineral formed during the burning of the brick. The character of the residues is seen in the photo-micrograph below (magnification 400 diams.). It will be seen that they are broken fragments of acicular crystals. Observations of the changes in powder density and porosity of the bricks after burning at various temperatures are being made. It is also intended to observe the influence of high temperature burning of firebricks on their resistance to corrosion by slags. The increase



× 400.

in the *mullite* ($3Al_2O_3 . 2SiO_2$) content of the brick implies an increase in the proportion of free silica, and a stage in burning may be reached where this may have a detrimental effect on the durability of the brick. It is probable from the experimental observations of Cobb and Hodsman[2], that the free silica in well-burned firebricks is present as silica glass or tridymite, as expansion curves show no indication of the presence of cristobalite. Some preliminary experiments on the resistance of aluminous firebricks to corrosion by molten glass at temperatures between 1,100°-1,500°C. indicate that the resistance of a brick burned at Cone 20 is less than that of a brick from the same batch burned at Cone 16.

Dept. of Refractory Materials,
University of Sheffield.

2 *Trans. Soc. Glass Tech.*, **3**, 201, 1919.

IV.—X-Ray Investigations of Clays and some other Ceramic Substances.

BY

ASSAR HADDING, Ph.D.

X-RAY ANALYSIS OF CRYSTALLINE SUBSTANCES: ATOM AND MOLECULE ANALYSIS.

X-RADIOGRAPHIC analysis is of two different kinds, either a "molecule" analysis or an "atom" analysis. By means of the "atom" analysis we determine the elements contained in the preparation, but we do not learn in what way the different elements are combined with each other.

The X-ray "molecule" analysis does not directly tell us the constituents of the preparation. It shows rather the structure of the substances, *i.e.*, the way in which the atoms are combined with each other. For instance, if we analyse a certain clay by these two methods, we find by the "atom" analysis that it contains silicon and aluminium, by the "molecule" analysis we find, on the other hand, that it consists of quartz and kaolin, because it shows the structure of these minerals. Thus the "atom" analysis corresponds to an ordinary chemical analysis, but it can never quite substitute this. The "molecule" analysis can be replaced by optical and other methods of investigation if the preparation is sufficiently coarsely crystalline. If, on the other hand, the substance is micro- or crypto-cristalline, only the X-radiographic method can be used. The minerals of a clay, for instance, can be determined only in exceptional cases by any other previously known method of investigation. *By means of the X-ray "molecule" analysis the determination of the minerals can be carried out with absolute certainty*, with certain restrictions only.

The "molecule" analysis is carried out in such a way that the preparation is irradiated with X-rays of known wave-length. The crystalline particles of the preparation then produce secondary X-rays. The directions of these rays is dependent upon the structure of the substance. Thus the photograph (or diagram) obtained when the rays blacken a photographic film is just as characteristic of the substance as its structure.

Are amorphous constituents to be found in clays?

Since amorphous substances do not have a regular structure, they neither produce secondary rays in the same way as the crystalline substances, nor do they possess characteristic X-radiograms. The "molecule" analysis, therefore, tells us in the first place whether the preparation is an amorphous substance or a crystalline one. It has been customary to consider an amorphous, colloidal mineral as forming the finer-grained portion of common clays. Upon examining several clays, however, I found that even the finest residue of the elutriation process is crystalline. Are there, then, no amorphous substances in clays? The question can not,

of course, be answered until thorough investigations have been carried out. It is not impossible that, during the alterations to the minerals which take place in the weathering of rocks and the formations of clays, amorphous substances were also produced. The amorphous state of solid substances is, however, more unstable than the crystalline. It is, therefore, *most natural that a "ripe" clay*—a clay in which the minerals are relatively stable—*should only contain crystalline minerals.*

X-ray analysis and classification of clays.

If we make allowance for laterite and other bauxitic clays, which in chemical respect differ from those of the temperate zones, we find that we have not hitherto been able to classify the clays mineralogically. The grain-size, the plasticity, the chemical composition and other physical and chemical qualities have, hitherto, been the determining principles for their classification. All these qualities are, however, entirely or partially dependent on the mineralogical composition of the clay. Hence this composition ought quite naturally to be the best basis for the classification of clays. As shown above, the X-ray "molecule" analysis is the only reliable method for the determination of the mineralogical composition of clays. The method will be found indispensable, both for the systematic arrangement and for the more practical investigation of clays.

The mineralogical composition of clays.

What is, then, the mineralogical composition of our common clays? It varies somewhat, as is evident from the chemical analysis as well as from other investigations. In a clay in the process of formation it ought to be of a different kind than in a "ripe" clay. The conditions of formation also play a great part. A young glacial clay may contain the powder of several different minerals, and it also may show traces of the alteration, which leads to a stabilization of the mineralogical composition of the clay. However, if we investigate the other clays of the temperate zones we shall find that they vary little qualitatively. There are, in reality, as far as my experience goes, *only three minerals* which occur in great quantity in these clays, namely, *quartz*, *kaolin* and *muscovite*. The character of the clay is determined (1) by the proportion in which the minerals occur in the clay; (2) by the size of the mineral-grains, and (3) by certain impurities (calcite, iron hydroxides, etc.).

The size of the grains is easily determined by elutriation and the purity of the clay by chemical analysis. The importance of these factors to the physical properties (plasticity, etc.), and to the usefulness of the clay for different purposes has been the object for a great many investigations, and it is also quite well known.

The mineralogical composition of clays is of importance to the physical qualities, because the various minerals have different structure, different form and different chemical constitution, even in cases where they have about the same chemical composition.

A clay with foliated minerals must show qualities differing entirely from those of a clay composed mainly of granular minerals. Differences in the mineralogical composition are always accompanied by differences in the chemical constitution (not in the chemical composition). Not only the temperature of dehydration, decomposition, melting and other physical-chemical qualities, but also the mechanical properties, such as plasticity, adsorptive capacity, etc., may change with the mineralogical composition.

I will give a few examples of the mineralogical composition of clays and of the X-ray "molecule" analysis, but first let me give a short account of the manner in which this analysis is performed.

The X-ray "molecule" analysis.

Test-piece: The substance is pressed into a cylindrical, gelatinous casing of 1-2 mm. diameter.

Camera: A cylindrical lead box has a centered holder for the test piece. The films are bent into cylindrical shape at the inner-wall of the box. The diameter of the film cylinder is about 50 mm.

X-ray tube: This is a metal tube with an iron or copper anti-cathode. (*Zeitschrift für Physik*, **3**, 369 and Hadding: The X-ray crystallographic apparatus and their use. Lund, 1921. Swedish).

Exposure: $\frac{1}{2}$—$1\frac{1}{2}$ hours, current 5–20 milliamperes; voltage 35,000—45,000 volts.

Films: X-ray films (Dr. Schleussner's).

The X-ray diagrams and their interpretation: The exposed and developed films, the X-radiograms, show a series of lines. Their grouping and strength varies for different minerals. Each special mineral has, however, as pointed out before, a diagram that is characteristic of the same. Such an X-radiogram can thus be used for the identification of minerals in the test piece. It may be pointed out that, *for the determination of the minerals, we do not need any calculation* (of the glancing angles, the grating constants, etc.). The simplicity of the method will make its practical utility so much the greater.

If the diagrams show a few strong lines they can be directly compared with diagrams of known minerals. If the lines are faint, or occur in great numbers, a direct comparison can hardly lead to a reliable determination. It is then necessary to measure the distances between the lines and, according to the measurements, make a table, or, still better, a graphical drawing of the diagram. This we use as the basis for the identification.

The identification is done in such a way that the drawing of the diagram is compared with the diagrams of known minerals. The comparison is the work of a moment if one has the necessary comparison-material. A few examples will illustrate the method.

Uncomplicated X-radiograms

Fig. 1 shows three uncomplicated X-radiograms in natural size. Fig. 2 is a graphic drawing of the quartz radiogram. In the former, the lines occur in the same order as in the right half of the

QUARTZ diagram. Iron anticathode. Film diameter 50·0 mm. Compare with the graphical drawing fig. 2.

Diagram of an ordovician clay from Tommarp, Sweden. MUSCOVITE diagram. Iron anticathode. Film diameter 50·3 mm.

Diagram of a molten clay. Höganäs-Billesholms A.B., Sweden. CORUNDUM diagram. Iron anticathode. Film diameter 49·9 mm.

NATURAL SIZE.

Fig. 1.

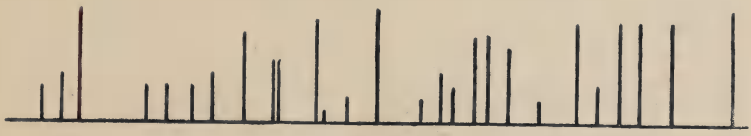


Fig. 2.

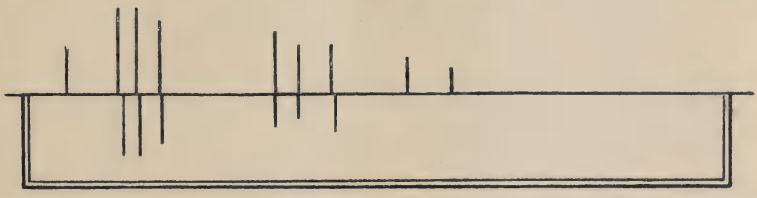


Fig. 3.

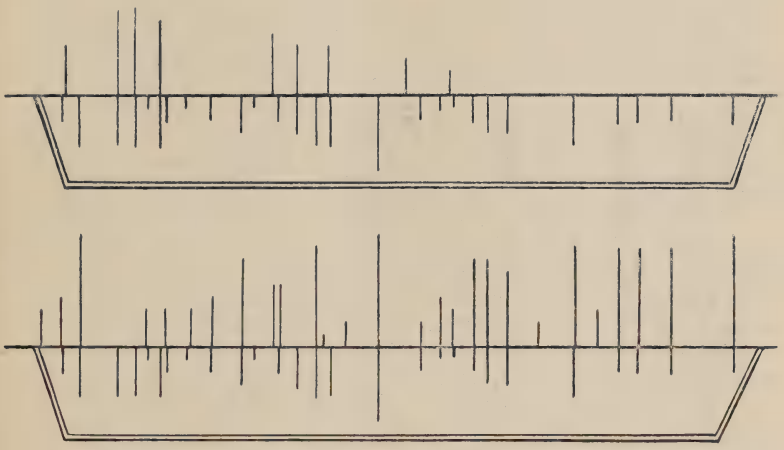


Fig. 4.

radiogram. The varying intensity of the black lines of the diagram is marked by different length of the lines in the drawing.

Fig. 3 shows the graphic drawing of two other, uncomplicated radiograms. The upper part of the figure illustrates a kaolin diagram, the lower half shows a clay diagram. The lines of the latter are drawn downwards. For the convenient determination of the minerals in a substance, the drawing of its diagram is made on a slip of paper, which can be put to the drawings of the diagrams of known minerals in the same way as the framed part here is put of the kaolin diagram. We find immediately that the clay, in spite of its X-radiogram being faint and incomplete, consists wholly of kaolin.

The middle diagram of Fig. 1 shows an Ordovician clay (from Tommarp, Sweden). There are only lines of muscovite. The glacial and postglacial clays sometimes show quartz lines only. However, the clay radiograms are generally complicated.

Complicated X-radiograms.

A complicated diagram is often interpreted as easily as an uncomplicated. The framed parts of Fig. 4 show the diagram of a fireclay (Lias, Höganäs, Sweden). In the upper picture the clay diagram is compared with a kaolin diagram, in the lower picture it is placed with a quartz diagram. We only have to cast a glance at the drawings to find that the clay consists of kaolin and quartz.

The above-mentioned clay radiogram was obtained from the coarsest product of elutriation. The diagram of the unelutriated clay showed weaker quartz lines and the finest product of elutriation gave a pure kaolin diagram.

For purposes of determination, an enrichment of one or other mineral may be of significance. Minerals that occur in only slight quantities in the sample will not generally be seen on the diagram before previous enrichment.

Amorphous substances cannot be determined by the above-mentioned method. However, their presence and also their relative quantity, ought to be tested.

X-ray "molecule" analysis of ceramic and other artificial products.

Not only mineral substances, but also ceramic and other artificial products can be investigated with the X-ray "molecule" analysis.

In Fig. 1 we find an X-radiogram of fused clay. The diagram is identical with that of corundum and thus the sample must be synthetic corundum. The structural and mineral alterations of a clay during the firing can be determined in the same way. The results may be interesting (*c.f.* Shearer: Results of an X-ray Investigation of the Crystalline Nature of China clays, TRANS., **22**, 106, 1923). However, I will not now discuss these problems.

The structural alterations of quartz during firing are also of interest. Natural tridymite has a diagram which cannot be distinguished from that of quartz, but the diagram of cristobalite is of a different structure. It is, therefore, natural that a low-fired silica (sample from Höganäs), gives the diagram of quartz, though the sample, optically investigated, is a tridymite aggregate. The high-fired silica (sample from Höganäs) shows the diagram of cristobalite, and I have found the same in quartz which had been fused twice.

Quartz, as a common component of clays, will also show the above-mentioned alterations in the clay products. In the diagram of a fired China-clay (from Ifö, Sweden), I observed the lines of cristobalite and kaolin. Thus the latter mineral, in spite of the high-firing, was structurally unaltered.

Among other X-ray molecule analyses of artificial products, I may also mention the analysis of Portland cement. According to this analysis, the quality of Portland cement is directly dependent on the degree of vitrification of the substance. The best Swedish Portland cement is entirely amorphous.

V.—Some Properties of Clay-Sillimanite Mixtures.

By H. S. Houldsworth, M.Sc.

(Department of Coal, Gas, and Fuel Industries, The University, Leeds).

CERAMIC literature contains few records of investigations of the chemical and physical properties of sillimanite and clay-sillimanite mixtures. English (*J. Soc. Glass Tech.*, **7**, 248-257, 1923) has described the results he obtained in a study of a mixture of sillimanite and 10 per cent. of ball clay. He found that such a body resisted attack by glass at 1,420°C. better than did a Stourbridge pot clay mixture, and that after firing to 1,400°C. the sillimanite mixture had a regular coefficient of expansion up to 800°C. Sillimanite is an expensive refractory, but if the properties of fireclays can be improved appreciably by the addition of much smaller quantities of sillimanite than English used in his experiments, its usefulness in industry might be considerably increased. Accordingly, the work described in this paper was undertaken in order to study the changes in the physical and chemical properties of a clay when varying percentages of sillimanite were incorporated with it.

The natural commercial sillimanite used in these experiments contained 32·9 per cent. SiO_2 and 64 per cent. Al_2O_3, Fe_2O_3, and TiO_2, and was graded as follows :—

								Per Cent.
Through	5-mesh	retained on		10	mesh in		..	11·8
,,	10	,,	,,	,, 20	,,		..	6·2
,,	20	,,	,,	,, 30	,,		..	17·5
,,	30	,,	,,	,, 50	,,		..	21·4
,,	50	,,	,,	,, 60	,,		..	6·8
,,	60	,,	,,	,, 80	,,		..	5·9
,,	80	,,	,,	,, 100	,,		..	2·4
,,	100	,,	,,	,, 120	,		..	2·9
,,	120	,,	,,	,, 150	,,		..	4·2
,,	150	,,	,,	,, 200	,,		..	2·9
,,	200							18·0

Test pieces were prepared from Farnley fireclay and sillimanite so as to contain 0, 20, $33\frac{1}{2}$, 50, and $66\frac{2}{3}$ per cent. respectively of sillimanite, as well as others consisting of 95 per cent. sillimanite and 5 per cent. ball clay and 90 per cent. sillimanite, and 10 per cent. ball clay, the Farnley fireclay and the ball clay being first ground to pass a 20 mesh standard I.M.M. sieve. The specimens were fired in a works kiln to cone 06, in 48 hours and cone 9 in 72 hours, some of the latter test-pieces being subsequently burned for 2 hours at cone 14 and cone 18 respectively in a laboratory gas-fired furnace, 3 hours being taken to attain the temperature.

The drying and firing shrinkages, porosity, true and apparent specific gravities, refractoriness, reversible thermal expansion, and resistance to solution by a soda-lime glass and a basic slag were determined.

Drying and Firing Shrinkages. The results obtained are collected in Table 1.

TABLE 1.

	Percentage Shrinkage				
	Drying	Cone 06	Cone 9	Cone 14	Cone 18
100% Farnley fireclay	5·72	5·77	6·72	8·29	10·74
80% ,, ,, +20% sillimanite	5·00	5·26	6·05	6·83	9·74
66⅔% ,, ,, +33⅓% ,,	3·47	3·62	4·26	5·05	7·67
50 % ,, ,, +50 % ,,	2·79	2·79	3·05	3·58	5·68
33⅓% ,, ,, +66⅔% ,,	1·78	1·78	2·26	2·52	—
90 % Sillimanite +10 % ball clay	2·10	2·36	2·70	2·96	3·15
95 % Sillimanite + 5 % ,, ,,	0·47	0·53	0·81	1·07	1·31

It will be seen that an increase in the percentage of sillimanite produces a decrease in the drying shrinkage and the contraction on burning (up to cone 18) of the mixtures. The difference in the drying shrinkages of the test pieces containing 10 per cent. and 5 per cent. of ball clay is noteworthy.

Porosity, True and Apparent Specific Gravity.

The results of these tests are shown in Table 2. The addition of sillimanite to the fireclay produces a more open structure in the body at the higher temperatures of burning. This would result in increased slag penetration if such bodies were exposed to attack by molten slags, and it would, presumably, be desirable in such circumstances to use with the sillimanite a bonding clay maturing at a lower temperature than those used in this investigation.

The open structure of these bodies would tend, however, to reduce strain due to rapid fluctuations of temperature.

Refractoriness. The refractoriness was determined in a gas-fired laboratory furnace and the results are collected in Table 3.

TABLE 3.

	Cone
100% Farnley fireclay	31
80% ,, ,, +20% sillimanite ..	32-
66⅔% ,, ,, +33⅓% ,, ..	32
50 % ,, ,, +50 % ,, ..	34-
33⅓% ,, ,, +66⅔% ,, ..	>36
90 % Sillimanite +10 % ball clay ..	>37
95 % ,, + 5 % ,, ,, ..	>37
100 % ,, ..	>37

It is evident that the presence of 50 per cent. or more of sillimanite in the clay-sillimanite mixture leads to a pronounced increase in the refractoriness of the body.

TABLE II.

POROSITIES, TRUE AND APPARENT SPECIFIC GRAVITIES.

	Cone 06.			Cone 9.			Cone 14.			Cone 18.		
	Porosity	Apparent sp. gr.	True sp. gr.	Porosity	Apparent sp. gr.	True sp. gr.	Porosity	Apparent sp. gr.	True sp. gr.	Porosity	Apparent sp. gr.	True sp. gr.
100% Farnley Fireclay ..	30·5	1·86	2·67	30·3	1·90	2·72	23·2	1·99	2·60	3·2	2·12	—
80% ,, +20% Sillimanite..	31·3	1·90	2·77	31·3	1·95	2·83	27·3	2·01	2·76	12·1	2·26	—
$66\frac{2}{3}$% ,, +$33\frac{1}{3}$% ,, ..	31·0	1·98	2·87	29·0	2·02	2·84	26·7	2·06	2·81	12·9	2·29	—
50% ,, +50% ,, ..	31·1	2·01	2·91	34·6	2·03	2·95	33·0	2·05	3·06	23·6	2·21	—
$33\frac{1}{3}$% ,, +$66\frac{2}{3}$% ,, ..	32·0	2·04	3·01	32·2	2·06	3·04	34·2	2·09	3·18	26·8	2·17	—
90% Sillim'nite + 10% Ball clay	35·8	2·08	—	34·4	2·09	3·19	38·0	2·12	3·41	34·5	2·11	—
95% ,, + 5% ,, ,,	35·8	2·02	3·15	35·6	2·06	3·21	39·1	2·02	3·31	39·6	2·05	3·40

Reversible Thermal Expansion.

The reversible thermal expansion of test-pieces 20 cms. long was determined by the method described previously (Houldsworth and Cobb, TRANS. **21**, 227-276, 1922), and the results are shown graphically in Figs. 1—4.

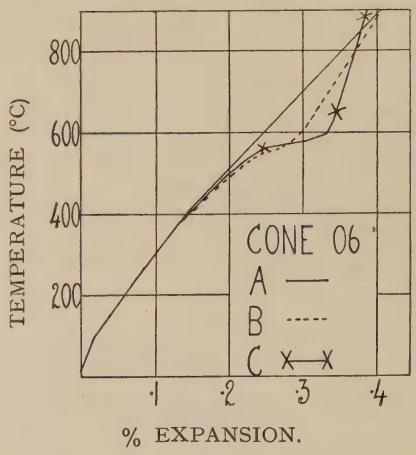


Fig. 1.
A. 95% Sillimanite + 5% Ball Clay.
B. 50% Sillimanite + 50% Fireclay.
C. Fireclay.

Cone 06. (See Fig. 1). The expansion from 15–900°C. of the test-piece containing 95 per cent. of sillimanite was almost the same as that of Farnley fireclay alone, or mixed with smaller quantities of sillimanite. The expansion of the sillimanite, however, was regular, whilst that of the clay showed the usual rapid expansion from 550–600°C., due to the inversion of α—β quartz. From 600–1,000°C. the rate of expansion of the sillimanite was considerably greater than that of the fireclay. The addition of sillimanite to the clay reduced the expansion from 550–600°C., and increased the expansion from 600–900°C.

Cone 9. (See Fig. 2). The reversible thermal expansion of the test-piece containing 95 per cent. of sillimanite was not altered by the increased temperature of firing and, from 15–1,000°C. was less than that of the Farnley clay alone by 0·9 per cent. The latter showed the characteristic increased rates of expansion from 100–200°C., and 550–600°C., whilst the expansion of the sillimanite was regular and, from 600–1,000°C., greater than that of the clay alone. The expansion curves of the other mixtures were intermediate between those of the sillimanite and fireclay.

Cone 14. (See Fig. 3). The reversible thermal expansion of sillimanite was not changed appreciably by firing to cone 14,

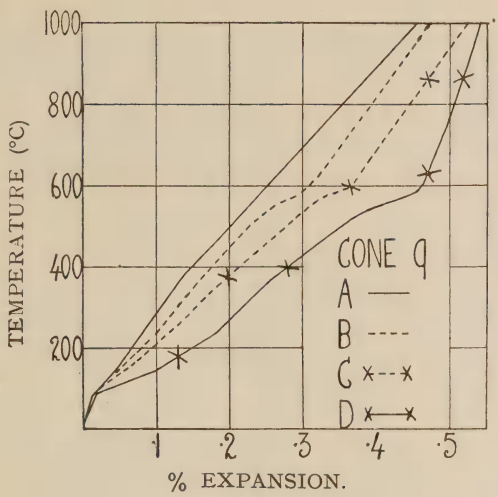


Fig. 2.
A. 95% Sillimanite + 5% Ball Clay.
B. 66⅔% Sillimanite + 33⅓ Fireclay.
C. 50% Sillimanite + 50% Fireclay.
D. Fireclay.

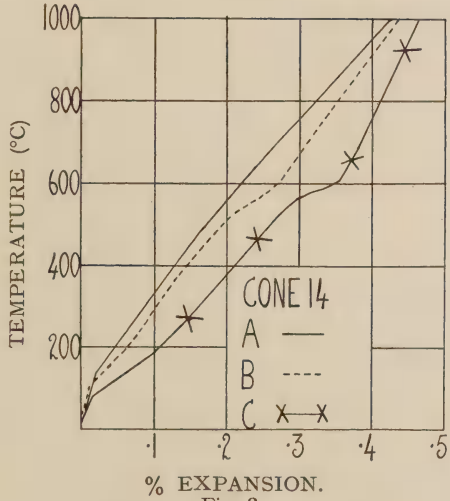


Fig. 3.
A. 95% Sillimanite + 5% Ball Clay.
B. 50% Sillimanite + 50% Fireclay.
C. Fireclay.

and was slightly less than that of the Farnley clay alone. The expansion of the latter was less than that shown by the cone 9

specimen, the change being due to a decreased expansion from 100–200°C. The expansion of the test-piece containing equal parts of clay and sillimanite was intermediate between that of sillimanite and that of Farnley fireclay.

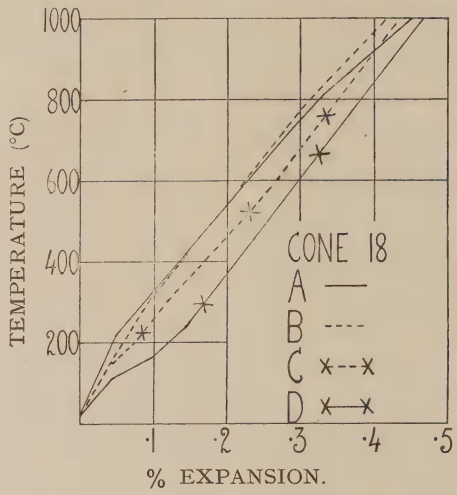


Fig. 4.
A. 95% Sillimanite + 5% Ball Clay.
B. 50% Sillimanite + 50% Fireclay.
C. $33\frac{1}{3}$% Sillimanite + $66\frac{2}{3}$% Fireclay.
D. Fireclay.

Cone 18. (See Fig. 4). The higher temperature of firing had not affected the reversible thermal expansion of the sillimanite. (The Farnley fireclay had now a regular coefficient of expansion from 200–1,000°C., the expansion in this range being slightly less than that of sillimanite. The free quartz in the clay had disappeared, having been taken into solution, solid or otherwise (Houldsworth and Cobb, *J. Soc. Glass Tech.*, **5**, 16–44, 1921). The reversible thermal expansion of a mixture of equal parts of clay and sillimanite was very regular from 15–1,000°C., and slightly less than that of the test piece containing 95 per cent. of sillimanite.

The results obtained show that the addition of sillimanite to a silliceous fireclay decreases the rate of expansion from 100–200°C., and from 500–600°C. by producing a more regular coefficient of expansion, and so would tend to diminish the strains due to rapid fluctuations of temperature.

Resistance to Slag Attack.

The attack of a molten slag upon the refractory lining of a furnace, etc., depends upon the solvent action of the slag upon the material and the penetration of the slag into the refractory brick or block. The first of these factors is often the more important,

as the attack of the hotter and more concentrated slag at the hot surface of the brick is more vigorous than that of the slag which has penetrated to the cooler parts of the brickwork. Various workers have suggested that a determination of the depression of the fusion temperatures of different refractories when mixed with the same proportion of the same slag should indicate the relative resistance of those refractories to the solvent action of the slag selected. Preliminary experiments by Howe (*J. Amer. Cer. Soc.*, **6**, 466–473, 1923), showed that the results of tests of this nature, considered in conjunction with porosity data, agreed better with the behaviour of refractories in use than did the more usual laboratory methods of determining resistance of slag attack. It appeared that this method was suitable for the determination of the relative degree of resistance of clay-sillimanite mixtures to the solvent action of slags.

The samples were ground until they passed a 100-mesh (I.M.M.) sieve, and thoroughly mixed with the desired proportion of finely ground glass or slag. A little gelatine solution was added, and cones were then shaped from the mixture. These were heated alongside standard Seger cones in a gas-fired laboratory furnace, 3–4 hours being taken to reach the fusion temperature in order to allow sufficient time for the interaction of the slag and the refractory. It was found that variations of an hour or so in the duration of the test did not affect the temperature of fusion of the mixtures.

Resistance to Attack by Soda-Lime Glass.

The soda-lime glass used was kindly supplied by Professor W. E. S. Turner and Mr. S. English, and was part of the batch used in the paper previously mentioned. The glass was prepared from the batch "sand 1,000, soda ash 325, limespar 228," and as broken cullet it showed only a light pale green colour. The results obtained are shown in Table 4.

TABLE 4.

CONE MELTING POINTS.

		Alone	+10% glass	+15% glass	+15% slag
100% Farnley clay	*A*	30	20+	17	14+
80% ,, ,, +20% sillimanite	*B*	31	26	17	14+
$66\frac{2}{3}$% ,, ,, +$33\frac{1}{3}$% ,,	*C*	32	26 } 30°	18 } 30°	15 –
50% ,, ,, +50% ,,	*D*	34	27	20	17
$33\frac{1}{3}$% ,, ,, +$66\frac{2}{3}$% ,,	*E*	>36	34 } 140°	30– } 140°	26+
10% Ball ,, +90% ,,	*F*	>37	>36	37	36+
5% ,, ,, +95% ,,	*G*	>37	>36	37	>36
100% Sillimanite	*H*	>37	>36	38	>36

It will be noted that when the percentage of sillimanite is increased from 50 to $66\frac{2}{3}$ per cent., the temperatures of fusion of mixtures containing 10 per cent. and 15 per cent. of glass respectively are each increased by 140°C., compared with the increase

of 30°C. between corresponding mixtures of *C* and *D*. Unfortunately, it was impossible in the furnace used to attain a temperature appreciably greater than cone 37, and so the actual fusion point of mixture *E* was not determined. The results suggest, however, that when the sillimanite present reaches $66\frac{2}{3}$ per cent., the resistance to attack by the glass is increased, whilst the temperature at which vigorous attack takes place is considerably increased. Mixtures of 90 per cent. sillimanite + 10 per cent. of ball clay appear to be very resistant to the solvent action of soda lime glasses and are not appreciably inferior to sillimanite alone in this respect.

Resistance to Attack by Basic Slag.

The resistance to attack by basic slag was also investigated, the composition of the slag used being:

	Per cent.
SiO_2	7·1
S	0·4
FeO	18·8
Al_2O_3	11·3
P_2O_5	11·1
MnO	3·6
CaO	40·6
MgO	3·7
H_2O	0·2
Unestimated	3·2

The fusion point of the slag was equivalent to that of cone 17. The results obtained with cones containing 15 per cent. of slag are shown in Table 4.

The increase in resistance to attack by the basic slag was, possibly, not so pronounced with the increase in the sillimanite content from 50–$66\frac{2}{3}$ per cent. as was found with the glass, but a very marked increase in resistance was shown by mixtures containing 90 per cent. sillimanite and 10 per cent. of ball clay. This increased resistance is due partly to the resistance of the sillimanite to attack by the slag, and partly to the decrease in the free silica content by the substitution of ball clay for the Farnley fireclay. It will be noticed that the fusibility of clay-sillimanite mixtures containing 50 per cent. of sillimanite, or less, when mixed with 15 per cent. of the slag, have a refractoriness equal to, or inferior to, that of the slag alone.

Summarising, it would appear that sillimanite bonded with 10 per cent. of ball clay is very resistant to attack by a soda lime glass or by a basic slag. Mixtures containing two-thirds sillimanite, and one-third fireclay, would appear to have a greater resistance to attack by soda lime glass, and possibly by basic slag, than fireclay alone, but smaller proportions of sillimanite do not appear to increase the resistance of clay-sillimanite mixtures to such attack.

SUMMARY.

The results of these experiments may be summarised thus:—

1. The addition of sillimanite to clay decreases the drying and firing shrinkages, increases the porosity at the higher temperatures of burning, and (when 50 per cent. or more is added), increases the refractoriness appreciably.
2. A mixture of 95 per cent. sillimanite + 5 per cent. of ball clay has a regular coefficient of expansion from 15–1,000°C., which is not affected appreciably by differences in the firing temperature up to cone 18. The rapid expansions shown by fireclays from 100–200°C. and from 500–600°C. are reduced by the addition of sillimanite. The expansion of a typical fireclay from 600–1,000°C. is less than that of sillimanite in the same range.
3. Sillimanite bonded with 10 per cent. of ball clay has a marked resistance to chemical attack by soda lime glasses and basic slag. Sillimanite-clay mixtures containing less than 50 per cent. of sillimanite are not appreciably more resistant to such attack than is fireclay alone.

In conclusion, I should like to express my thanks to Mr. P. F. Summers, A.R.S.M., of this Department, for the analysis of the basic slag used.

VI.—The Influence of Exposure on the Chemical and Physical Properties of Certain Fireclays.

BY

W. Hugill, M.Met. and W. J. Rees, B.Sc. (Tech.), F.I.C.

INTRODUCTION.

THE natural weathering of rocks and minerals has been the subject of numerous investigations. General summaries of the results achieved, considered from several aspects, are to be found in such works as those of Clarke[1], Merrill[2], Hilgard[3], Bonney[4], Geikie[5], and Glinka[6]. The only observations of which we are aware, dealing especially with fireclay, are those published by Bywater[7]. Not much endeavour to place the time factor in natural weathering upon a quantitative basis appears to have been made, most emphasis having been laid upon the chemical and physical changes produced during long periods, whose duration cannot be more than approximately estimated.

A decided preference is expressed by manufacturers of refractory materials for the outcrop portion of fireclay beds. Here the clays have been subjected to the attack of rain and its dissolved substances ; to percolating ground waters ; to freezing and thawing, and other weathering agencies for a prolonged period. Taking into account the relatively slow alteration of the locus of the outcrop, we may consider that such clay as mined reveals the cumulative effect of weathering for at least several hundred years. In an endeavour to bring clay obtained from further underground into a similar condition, it is often exposed at the surface for several months before using. This practice, however, is not generally adopted, nor uniformly even when treating the same clay.

The purpose of the experiments detailed below was to investigate the nature of the changes occurring in the case of fireclays exposed for a fixed period, during which the meteorological conditions were recorded.

Location and General Character of the Clays Studied.

Samples of fireclay were taken from three localities as follows :

No. 1. This forms the seat earth of the Lower Busty Seam, Co. Durham. It is a light grey, somewhat sandy, micaceous clay[8].

No. 2. A dark coloured, compact, fine-grained clay from the well-known Pot Clay Bed of the Sheffield district.[9]

No. 3. A light grey, very sandy and micaceous variety from the same stratum as No. 2, but from a different locality.

Gibson[10] refers to such changes in the character of the Sheffield Pot Clay as that shown between samples 2 and 3.

Preliminary Treatment.

About five kilos. of each clay were taken. This was broken into pieces about 2 inches in diameter, well mixed, and each sample divided into two portions. One of these was used for making a series of bricks, the other was reserved for exposure to the weather.

Mode of Exposure.

The clay was spread evenly over the bottom of a wooden box, 12 in. wide by 24 in. in length. A piece of fine muslin was fastened over the top to keep out extraneous matter. The box and contents were supported on two bricks in the open air for twelve months. Sample No. 1 was exposed at Guisborough during 1921, Nos. 2 and 3 on the roof of the Department of Applied Science during the year 1922-1923.

Meteorological Conditions.

These are summarised in Table 1. 23·3 gallons of rain per-

TABLE I.
SUMMARY OF WEATHER CONDITIONS.

SAMPLE No. 1. Exposed from Jan. 1st, 1921 to Dec. 31st, 1921, at Guisborough.								
Month	Rain ins.	No. of Rainy days	Highest and lowest temp. for month °F.	No. of days at or below 32°F.	Hours of Sunshine	No. of days with more than 0·1 hr. Sunshine	SO_4 parts per million	Cl. parts per million
Jan. ..	2·8	22	57–29	2	26·3	13	10	37
Feb. ..	0·4	7	57–30	2	43·5	16	28	19
Mar. ..	2·2	19	64–30	1	80·2	20	29	15
Apr. ..	0·9	14	68–29	2	171·7	29	10	5
May ..	1·3	18	75–33	0	219·5	30	12	11
June ..	0·3	5	86–40	0	211·8	29	7	4
July ..	0·5	8	89–42	0	194·0	30	9	8
Aug. ..	5·0	21	80–43	0	144·1	29	41	30
Sept. ..	0·8	9	79–45	0	168·0	28	13	7
Oct. ..	2·3	10	73–36	0	121·9	29	25	15
Nov. ..	1·7	9	58–25	8	48·7	15	16	13
Dec. ..	4·2	22	57–26	4	35·5	19	28	40
Totals	22·4	164	—	19	1465·2	287	228	204

TABLE 1.—*continued*,

SAMPLES Nos. 2 & 3. Exposed from Feb. 18th, 1922 to Feb. 17th, 1923, at Sheffield.

Month	Rain ins.	No. of Rainy days	Highest and lowest temp. for month °F.	No. of days at or below 32°F.	Hours of Sunshine	No. of days with more than 0·1 hr. Sunshine	SO_4 parts per million	Cl. parts per million
Feb. ..	4·6	21	55–31	4	72·0	20	67	18
Mar. ..	2·0	21	57–32	4	50·8	23	40	10
Apr. ..	3·8	18	56–27	5	1161·1	26	50	13
May ..	6·0	11	75–36	0	223·5	29	55	15
June ..	0·6	5	80–43	0	195·6	27	20	5
July ..	3·1	19	74–43	0	143·5	27	28	7
Aug. ..	7·7	18	71–44	0	142·6	28	50	16
Sept. ..	2·8	17	68–41	0	70·7	26	29	8
Oct. ..	1·0	16	64–32	1	80·2	27	20	5
Nov. ..	2·2	14	55–31	2	61·8	24	25	7
Dec. ..	4·5	23	54–31	0	39·7	21	49	12
Jan. ..	1·5	21	54–32	1	49·3	21	28	8
Totals	39·8	204		17	1245·8	299	461	124

colated through sample No. 1, and contained 372 grains of SO_4 and 333 grains of Cl (as chlorides). 39·8 gallons passed through each of the samples exposed at Sheffield and contained 1,285 grains of SO_4 and 346 grains of Cl. The methods of analysis were those of Thresh[11]. The composition of Sheffield rain water was made the subject of a report by Wynne in 1914-1915[12].

Chemical Analysis.

The chemical compositions of the three clays in the unexposed and exposed states are shown in Table II, the methods used being those recommended by the Ceramic Society[13].

On comparing the analyses it is to be seen that :—

Loss on ignition increases in all cases.

SiO_2 and TiO_2 remain practically unchanged.

Al_2O_3—a marked increase is shown by the Durham clay, the Sheffield clays showing only a slight increase.

Fe_2O_3—all the samples show a slight decrease.

TABLE II.

CHEMICAL ANALYSES.

Sample No.	1 Unexposed	1 Exposed	2 Unexposed	2 Exposed	3 Unexposed	3 Exposed
SiO_2	60·86	59·82	51·15	52·01	63·43	63·15
TiO_2	1·00	0·94	0·59	0·55	0·47	0·46
Al_2O_3	26·00	28·79	29·96	30·31	19·89	20·01
Fe_2O_3	1·14	1·00	2·78	2·35	2·86	2·76
CaO	0·20	tr.	0·51	0·51	0·72	0·69
MgO	1·71	0·52	0·94	0·50	1·04	0·98
Alkalies as K_2O ..	3·36	0·91	1·15	0·93	2·05	1·90
Loss on ignition ..	6·20	7·05	12·76	13·05	9·25	10·01
Fe S_2	n.d.	n.d.	0·48	0·32	0·68	0·65
	100·47	99·03	100·32	100·53	100·39	100·61
Total Soluble Salts	1·54	tr	0·90	0·47	0·96	0·48
Soluble SO_3 ..	1·03	tr	0·22	0·18	0·28	0·16
Refractoriness, Cone No. ..	28	29–30	31–32	32	29	29–30

CaO—this remains constant in the aluminous clay, but decreases in the more siliceous clays.

MgO—decreases in all cases, but most markedly in the case of the Durham clay. This sample had 1·54% of $MgSO_4$ present.

Alkalis—in all three cases there is a reduction, but it is greatest in the Durham clay.

Soluble Salts—Though a decrease occurs in all three samples, the removal of the soluble magnesium sulphate in the Durham sample is the most important feature.

FeS_2—This constituent was not determined in the Durham clay. The notable change undergone during the exposure of No. 2 sample will be dealt with in connection with the heavy mineral crops of the clays. The amount of pyrites present was determined by the method used by Radley[14].

The refractoriness was increased by exposure in all cases.

Mechanical Analysis.

The sedimentation method described by Hall[15] was used except that settling velocities of 0·5, 2·0 and 7·0 mms/sec. correspond-

TABLE III.

MECHANICAL ANALYSES.

Sample No.	1 Unexposed	1 Exposed	2 Unexposed	2 Exposed	3 Unexposed	3 Exposed
<0·50—>0·10 mm.	8·9	4·0	1·5	1·6	41·5	41·5
<0·10—>0·05 ,,	10·4	17·0	1·1	1·2	11·1	10·9
<0·05—>0·01 ,,	32·3	27·0	18·0	22·0	13·1	13·0
<0·01 ,,	48·4	52·0	79·4	75·2	34·3	34·6
"HEAVY MATERIALS" IN THE ABOVE GRADES.						
<0·50—>0·10 mm.	n.d.	n.d.	0·35	0·25	0·75	0·73
<0·10—>0·05 ,,	n.d.	n.d.	0·52	0·25	0·05	0·02
<0·05—>0·01 ,,	n.d.	n.d.	0·04	0·02	n.f.	n.f.

ing to quartz grain sizes of 0·01, 0·05 and 0·10 mm. were adopted. No very significant changes occurred in the relative proportions of the grades by exposure. The results are given in Table III.

The "heavy minerals" in the sand and silt grades of clays 2 and 3 were separated by means of bromoform (S.G. 2·90). They were examined under the microscope and their nature and distribution is shown in Table IV. The chief "heavy mineral" in clay No. 2 is marcasite, identified by its colour (being more greenish than pyrites) and by crystal shape and aggregation. This was considerably reduced by exposure for twelve months. A considerable part of the heavy crop of clay No. 3 consisted of pyrites (showing cube and octahedral faces mainly) as mentioned by Allen, Crenshaw, Johnston and Larsen[16]. The amount of sulphide

TABLE IV.

		Hornblende	Zircon	Rutile	Staurolite	Pyrites	Marcasite	Chlorite
No. 1	Unexposed ..		Not	deter-	mined			
	Exposed ..		Not	deter-	mined			
No. 2	Unexposed ..		+			+	+	
	Exposed ..		+			+	+	
No. 3	Unexposed ..	+	+	+	+	+		+
	Exposed ..		+	+	+	+		

minerals in this clay was not so much reduced by exposure. An examination of Table IV. shows that although clays 2 and 3 occur at the same geological horizon they are quite distinct in character and represent different phases in deposition.

Preparation of the Bricks.

In each case (before and after exposure) the sample was ground to pass a 30-mesh sieve, moistened with water, and allowed to stand for 24 hours. Then more distilled water was added until the batch was of the desired consistency. This was measured by means of a Vicat needle. When a needle of 300 grams weight and of 1 sq. mm. cross-section sank through 4 cms. of the moist clay in five minutes it was considered to be of the right consistency. These figures are the ones adopted by Langenbeck[17] for determining the plasticity of clays. The amount of water added plus that present as hygroscopic moisture was as follows :—

TABLE V.

	Unexposed.	Exposed.
Clay No. 1	26·48	25·59
,, No. 2	23·54	22·45
,, No. 3	20·31	20·33

From these figures it will be observed that with Nos. 1 and 2 clays less water is required for the exposed as compared with the unexposed clays.

Working Properties of the Clays.

No. 1. Worked somewhat more smoothly after exposure, but was less plastic. *c.f.* also Searle[18].

No. 2. Exposure transformed this clay into a very tough, spongy form, much more difficult to work than in the newly-mined state.

No. 3. The working qualities were very much improved by exposure.

Drying Contraction.

Twelve bricks $4'' \times 1\frac{1}{2}'' \times \frac{3}{4}''$ were made from each series, and marked with parallel lines 3″ apart. They were then allowed to dry at room temperature for three days. Afterwards they were dried at 105-110°C. in an air oven. The linear contraction due to drying was as shown in Table VI.

TABLE VI.

	Unexposed.	Exposed.
No. 1	6·25%	5·00%
No. 2	7·67%	6·67%
No. 3	5·70%	5·34%

All three clays show less contraction after exposure.

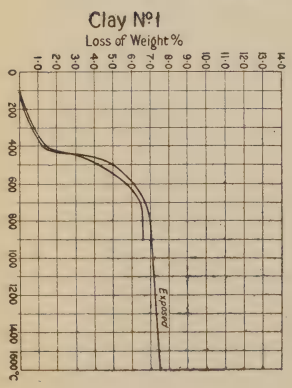
Loss of Weight due to Firing.

Half bricks were used for temperatures from 200° to 700°C.,

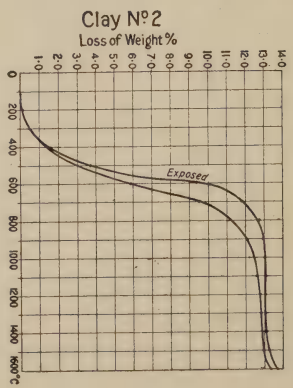
TABLE VII.
LOSS OF WEIGHT PER CENT.

Temperature °C.	1 Unexposed	1 Exposed	2 Unexposed	2 Exposed	3 Unexposed	3 Exposed
200	0·21	0·19	0·09	0·10	0·12	0·11
300	0·75	0·60	0·59	0·59	0·60	0·62
400	1·40	1·19	1·38	1·50	1·41	1·40
500	4·20	5·00	2·99	3·70	2·70	2·69
600	5·65	6·18	5·89	9·34	4·10	4·00
700	6·47	6·70	9·52	11·82	5·50	5·60
800	6·59	6·99	11·13	12·73	6·68	6.71
900	6·61	7·08	12·05	12·94	7·22	7·09
1000	not determined	7·17	12·24	12·94	7·43	7·27
1100		7·20	12·66	13·03	7·49	7·39
1200		7·25	12·79	13·06	7·58	7·44
1300		7·30	12·84	13·06	7·69	7·53
1400		7·37	12·85	13·09	7·90	7·62
1500		7·42	12·96	13·23	8·00	7·80
1600		7·50	13·41	13·68	7·89	8·10

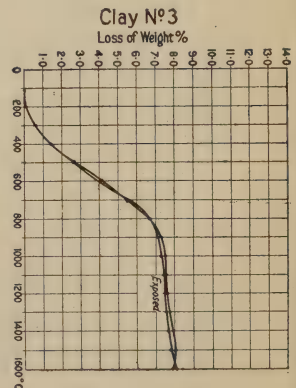
whole bricks for temperatures 800° to 1,600°C. A mercury thermometer was used up to 300°C., a Pt-Pt.Rh. thermo-couple up to 1,200°C. and a Mesuré and Noel optical pyrometer checked by means of Seger Cones from 1,300° to 1,600°C. After firing the bricks were again weighed. The results are recorded in Table VII. and expressed graphically in Curves 1, 2, and 3.



Curve No. 1.

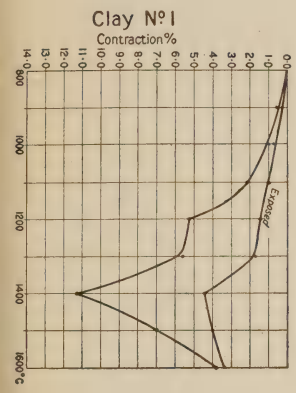


Curve No. 2.



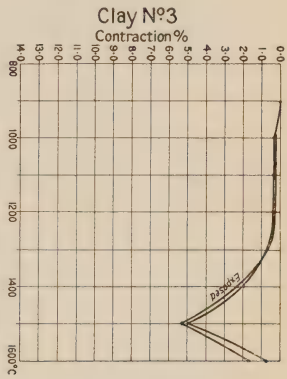
Curve No. 3.

Clay No. 2 showed the widest divergence in the rate at which weight is lost between 450° and 650°C.



Curve No. 4.

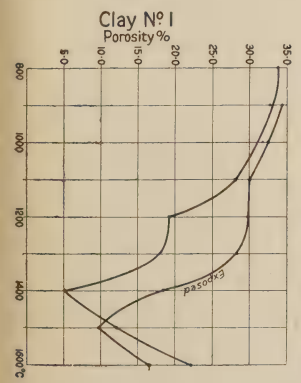
Curve No. 5.



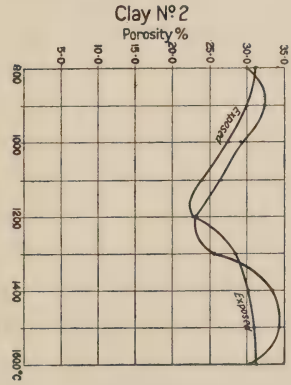
Curve No. 6.

Firing Contraction.

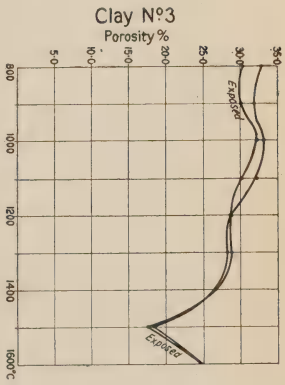
In Table VIII. are given the linear contractions for each series. Clays No. 1 and 3 give less contraction in the weathered than unweathered condition. Clay No. 2 behaves in a peculiar manner. It contracts up to 1,100°C. and then expands up to 1,300°C. After this temperature it contracts agains and continues to do so up to 1,600°C. Much surface cracking takes place in the bricks made from this clay in the unexposed state. The exposed sample shows very little of this "crizzling" effect.



Curve No. 7.



Curve No. 8.



Curve No. 9.

Density, Porosity and Volume Changes.

Table IX. gives the values obtained for each series. In the exposed and unexposed series for clay No. 3 the values do not

TABLE VIII.

FIRING CONTRACTION PER CENT.

Temperature °C.	1 Unexposed	1 Exposed	2 Unexposed	2 Exposed	3 Unexposed	3 Exposed
800	0·0	0·0	1·0	1·0	0·0	0·0
900	0·5	0·3	2·0	2·0	0·0	0·0
1000	1·0	0·7	4·0	4·0	0·3	0·3
1100	2·1	1·0	4·7	4·3	0·35	0·3
1200	5·3	1·4	+0·5	+0·6	0·4	0·35
1300	5·6	1·7	+1·3	+1·3	0·7	0·7
1400	11·3	4·4	0·7	0·35	2·0	2·3
1500	7·0	4·0	1·7	1·3	5·0	5·3
1600	3·8	3·4	3·3	3·0	0·7	1·7

In the bricks marked + an expansion took place.

depart much from each other, and on the whole the density, porosity and volume changes agree with each other at high firing temperatures. Both series bloat to a similar extent.

Clay No. 1 shows slower decrease in porosity, a higher temperature for minimum porosity, and less bloating in the exposed series. The more aluminous and closer-grained sample No. 2 shows several anomalies which, together with the phenomenon of a second contraction mentioned earlier, are being investigated further. Firth, Hodkin and Turner[19] in their investigation of clays fired to several temperatures get irregularities in powder density with increase of temperature in the case of the more aluminous clays.

Microstructure.

On the whole the microstructure of the bricks made from unexposed clays shows a greater proportion of melt than those made from clay which has been exposed to the weather. This is notable in the case of Clay No. 1. At 1,600°C. the unexposed material gives a glass containing bubbles, as shown in Fig. 17, whereas the corresponding brick made from the exposed material gives a more solid structure, Fig. 18.

In samples 1 and 3 there is a better disposition of the coarser clay particles after exposure, which probably accounts for the improvements in working properties; sample No. 2 does not show a change of this character in the exposed clay.

Conclusions.

Exposure to the weather removes impurities in the clay to a variable extent, depending on their chemical and physical character-

istics. It improves the working properties of Nos. 1 and 3 clays (which are siliceous), but in the case of No. 2 clay (which is more aluminous) whilst some impurities are removed, the general properties, and in particular the workability, are not materially improved by exposure.

TABLE IX. (A).

SAMPLE NO. 1 UNEXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity %
800		1·72	2·60	33·7
900		1·74	2·60	32·7
1000		1·76	2·59	31·9
1100		1·87	2·60	28·1
1200		2·07	2·56	19·1
1300		2·07	2·53	18·9
1400		2·40	2·53	5·1
1500		2·16	2·46	12·2
1600		1·88	2·41	22·2

SAMPLE NO. 1 EXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity %
*800	—	—	—	—
900		1·76	2·62	34·3
1000		1·76	2·60	32·5
1100		1·84	2·61	30·0
1200		1·79	2·55	29·9
1300		1·76	2·45	28·2
1400		2·00	2·45	18·4
1500		2·18	2·42	9·8
1600		1·93	2·31	16·5

*This brick decomposed into flakes when boiled in water.

TABLE IX. (B).
SAMPLE NO. 2 UNEXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity%
800	53·8	1·68	2·40	30·0
900	57·2	1·66	2·50	32·4
1000	54·0	1·77	2·50	29·2
1100	49·5	1·85	2·53	26·5
1200	47·5	1·96	2·55	23·2
1300	53·3	1·77	2·38	25·6
1400	59·5	1·58	2·37	33·4
1500	54·0	1·66	2·53	34·3
1600	53·0	1·80	2·58	30·5

SAMPLE NO. 2 EXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity%
800	59·0	1·75	2·54	31·1
900	55·8	1·75	2·50	30·0
1000	54·8	1·81	2·50	27·6
1100	51·8	1·86	2·57	23·8
1200	52·0	1·99	2·58	23·0
1300	60·9	1·73	2·42	28·5
1400	61·9	1·62	2·32	30·2
1500	61·7	1·68	2·47	31·1
1600	57·8	1·76	2·56	31·2

TABLE IX (C).
SAMPLE NO. 3 UNEXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity%
800	66·0	1·70	2·53	32·9
900	66·0	1·73	2·54	31·9
1000	66·2	1·72	2·57	33·1
1100	63·5	1·75	2·58	32·2
1200	63·6	1·81	2·54	28·7
1300	60·3	1·84	2·56	28·2
1400	63·6	1·89	2·57	26·5
1500	55·5	2·06	2·52	18·3
1600	64·8	1·84	2·44	24·6

TABLE IX (c)—*continued.*
SAMPLE NO. 3 EXPOSED.

Temp. °C.	Volume cc.	Apparent density	Powder density	Porosity%
800	66·7	1·76	2·53	30·4
900	66·7	1·77	2·53	30·0
1000	66·5	1·75	2·58	32·2
1100	66·1	1·81	2·57	30·1
1200	63·8	1·83	2·59	28·8
1300	62·8	1·87	2·55	28·8
1400	62·6	1·88	2·56	26·6
1500	56 3	2·09	2·50	17·6
1600	63·4	1·85	2·45	24·5

CLAY NO. 1.

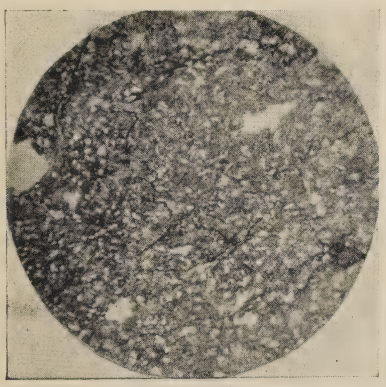


Fig. 1. Fireclay. O.L. ×20.

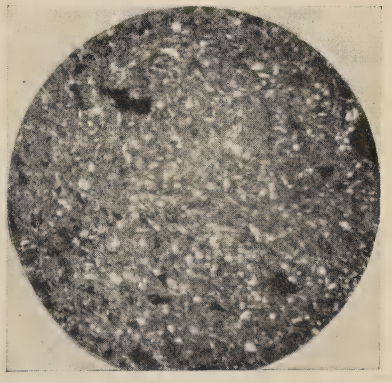


Fig. 2. Fireclay. Crossed Nicols. ×20

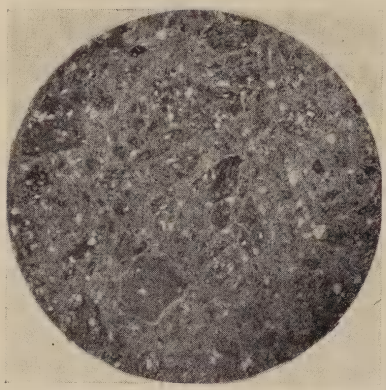


Fig. 3. Unweathered Series. O.L.
Brick fired at 800°. ×20.

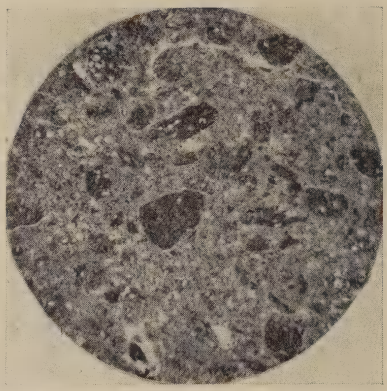


Fig. 4. Weathered Series. O.L.
Brick fired at 800°. ×20.

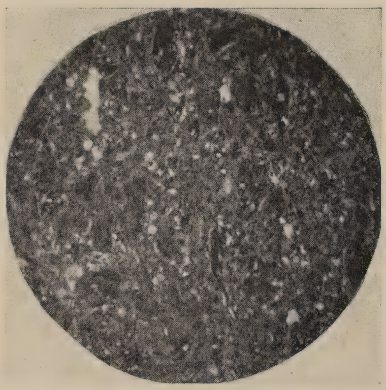


Fig. 5. Unweathered Series.
O.L. ×20.
Brick fired at 900°.

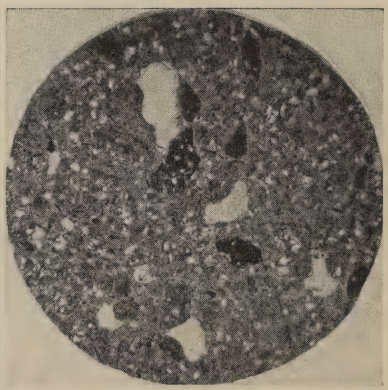


Fig. 6. Weathered Series.
O.L. ×20.
Brick fired at 900°.

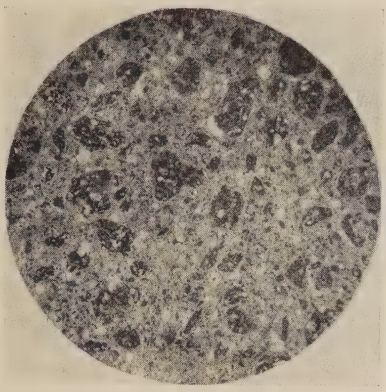


Fig. 7. Unweathered Series.
O.L. ×20.
Brick fired at 1000°.

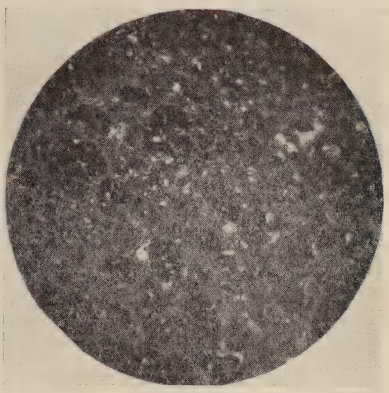


Fig. 8. Weathered Series.
O.L. ×20.
Brick fired at 1000°.

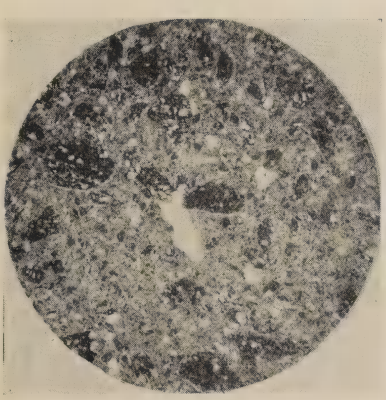


Fig. 9. Unweathered Series.
O.L. ×20.
Brick fired at 1100°.

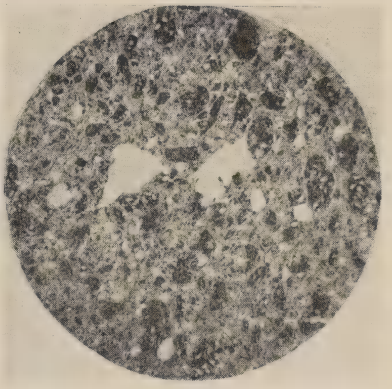


Fig. 10. Weathered Series.
O.L. ×20.
Brick fired at 1100°.

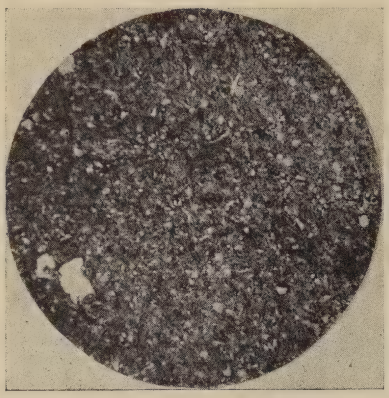


Fig. 11. Unweathered Series.
O.L. ×20.
Brick fired at 1200°.

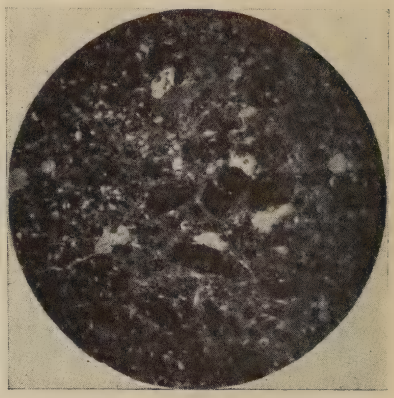


Fig. 12. Weathered Series.
O.L. ×20.
Brick fired at 1200°.

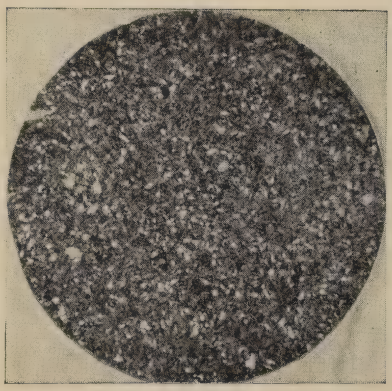


Fig. 13. Unweathered Series.
O.L. ×20.
Brick fired at 1300°.

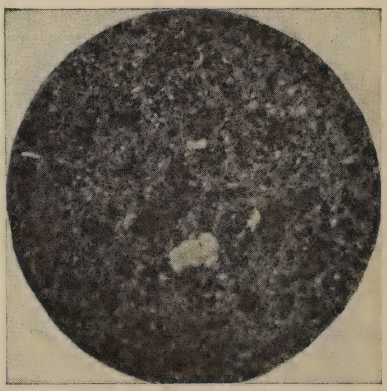


Fig. 14. Weathered Series.
O.L. ×20.
Brick fired at 1300°.

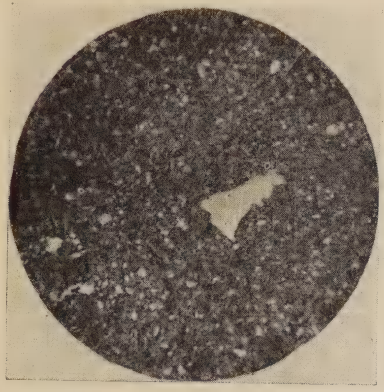


Fig. 15. Unweathered Series.
O.L. ×20.
Brick fired at 1400°.

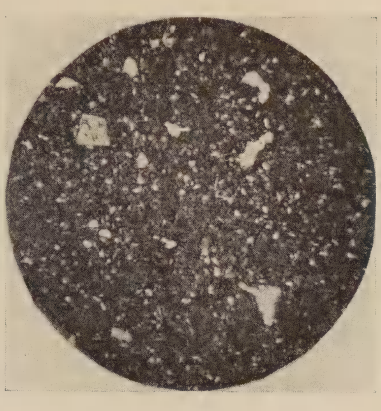


Fig. 10. Weathered Series.
O.L. ×20.
Brick fired at 1400°.

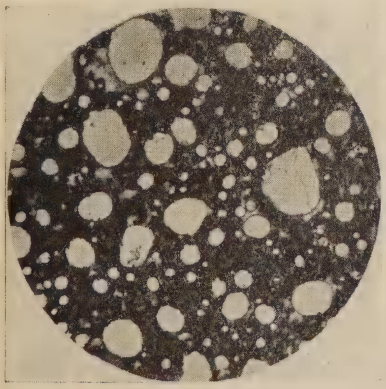


Fig. 17. Unweathered Series.
O.L. ×20.
Brick fired at 1600°.

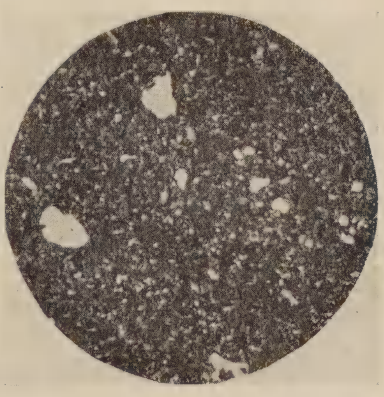


Fig. 18. Weathered Series.
O.L. ×20.
Brick fired at 1600°.

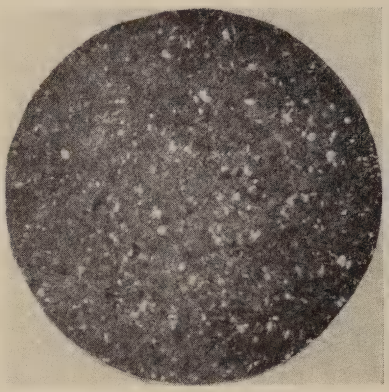


Fig. 19. Unweathered Series.
×Ni. ×20.
Brick fired at 800°.

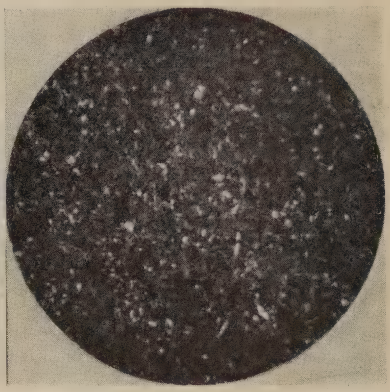


Fig. 20. Weathered Series.
×Ni. ×20.
Brick fired at 800°.

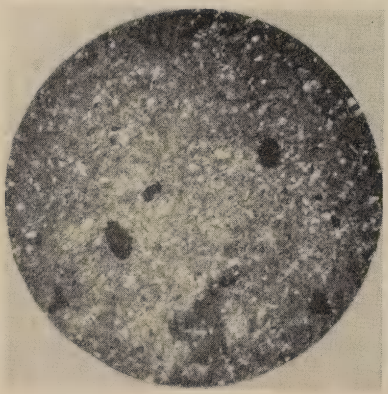


Fig. 21. Unweathered Series.
×Ni. ×20.
Brick fired at 900°.

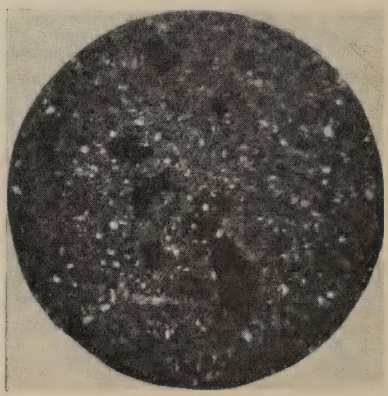


Fig. 22. Weathered Series.
×Ni. ×20.
Brick fired at 900°.

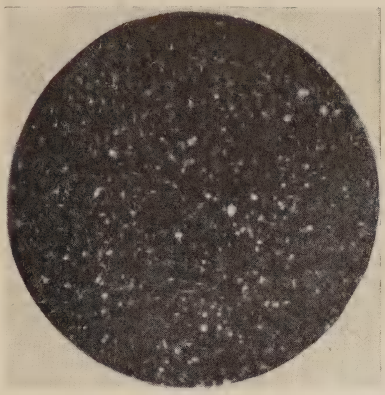


Fig. 23. Unweathered Series.
×Ni. ×20.
Brick fired at 1000°.

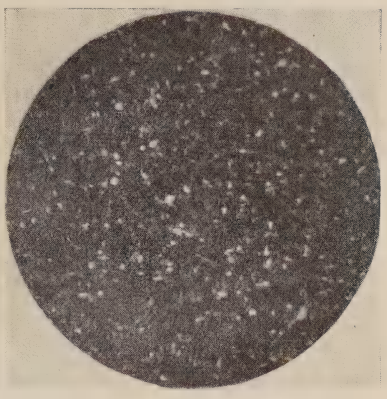


Fig. 24. Weathered Series.
×Ni. ×20.
Brick fired at 1000°.

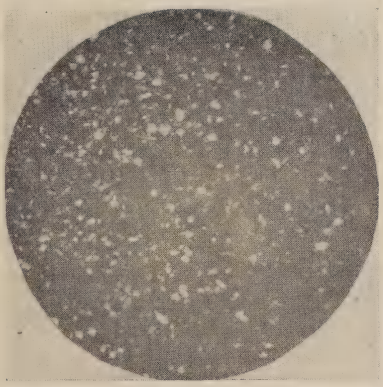


Fig. 25. Unweathered Series.
×Ni. ×20.
Brick fired at 1100°.

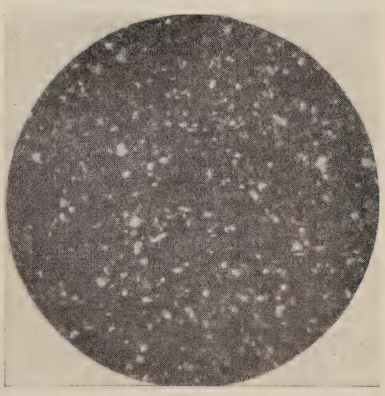


Fig. 26. Weathered Series.
×Ni. ×20.
Brick fired at 1100°.

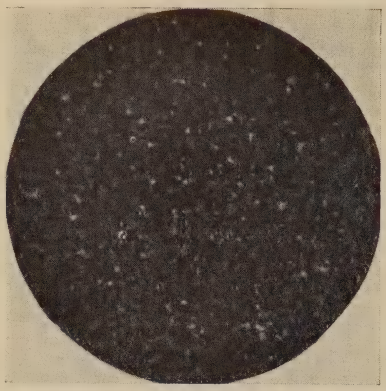


Fig. 27. Unweathered Series.
× Ni. × 20.
Brick fired at 1200°.

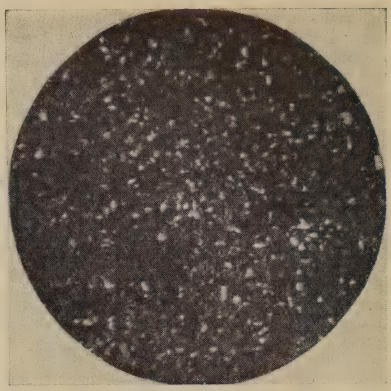


Fig. 28. Weathered Series.
× Ni. × 20.
Brick fired at 1200°.

Fig. 29. Unweathered Series.
× Ni. × 20.
Brick fired at 1300°.

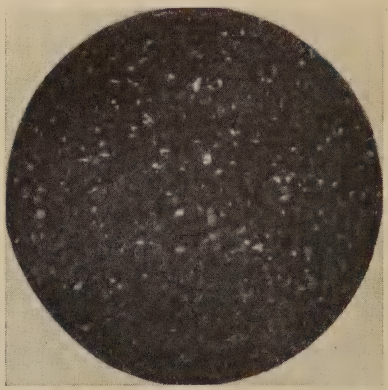


Fig. 30. Weathered Series.
× Ni. × 20
Brick fired at 1300°.

Additional Experiments on the Mechanism of the Decomposition of Mineral Sulphides, with Particular Reference to Possible Bacterial Action.

Three flasks (one litre) marked *A*, *B* and *C*, were taken. Into each of these 500 cc. of distilled water was placed, and the whole sterilised by boiling on three successive days. To each flask when cold 1 gram of finely-powdered marcasite was added.

Flask *A*. This was inoculated with 0·1 cc. of ochreous water from a ganister mine and to Flask *C* 0·2 cc. of the same water was added. Flask *B* was not inoculated. They were all securely plugged with sterile cotton wool and allowed to stand at room temperature for six months. Then the amount of soluble sulphates was determined in each. The results were as follows :—

	A	*B*	*C*
SO_3 ..	·1095	·0735	·0910

A piece of pyritic shale which was showing signs of decomposition, and a considerable amount of white efflorescence of sulphates was taken. This was broken in two, one part being set aside in its original condition, the other washed to remove the white, feathery efflorescence, and then sterilised at 110°C.for 24 hours.

While further decomposition is at present taking place in the original portion, that which was sterilised is still unaffected, although it has been kept about one month.

Further experiments on this subject are in progress.

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VII.—Note on the Storage of Silica Refractories.

W. J. Rees, B.Sc. (Tech.), F.I.C.

CARE is usually exercised in the storage of bricks or other refractory goods made from silica. Cases of considerable alteration in the physical behaviour (particularly the mechanical strength and spalling tendency) of silica bricks which have been stored under unsuitable conditions have occasionally come under my notice. For instance, a batch of silica bricks which had been stored in the open for 6 months (October to April) spalled badly in use, whilst normal freshly delivered bricks of the same make, and having the same texture, specific gravity, etc., were satisfactory. The good bricks had a cold crushing strength of 3,000 lbs. per sq. in., whilst that of the stored bricks was only 2,200 lbs. per sq. in. The bricks in both tests were dry and were placed on end in the testing machine ; the ends being previously made plane and parallel.

Observations have been made on two batches of commercial silica bricks, one of coarse texture and the other of moderately fine texture. The fresh bricks had the following chemical composition and physical properties :

	Coarse textured brick.	Fine textured brick
Silica	95·34%	94·90%
Alumina	1·02	1·34
Iron oxide	0·79	0·88
Titanium oxide	0·21	0·31
Lime	1·91	1·84
Magnesia	0·18	0·16
Alkalies (as K_2O)	0·46	0·51
	99·91	99·94
Apparent density	1·76	1·79
True density	2·45	2·38
Porosity	29%	25%
Refractoriness	Cone 33	Cone 32
Average of 3 Tests } Cold crushing strength ..	2400 lbs. per sq. in.	2900 lbs. per sq. in.

12 bricks of each batch were then placed in the open, unprotected from the weather, for the months February to May. (Snow in the early part of this period and frequent rainy and windy days). Bricks from each batch were also stored under approximately the same temperature conditions, but protected from the weather, and a further batch was placed in a warmed store-room.

The mechanical strength of these batches of bricks at the end of the 4 months was :—

	Coarse texture lbs.	Fine texture per sq. in.
Unprotected from weather (average of 3 bricks)	1400	2150
Protected ,, ,, ,, ,, ,,	2100	2600
Kept in store-room ,, ,, ,,	2350	2900

The bricks were air-dried before testing.

The fine-textured bricks stored in the open showed no external signs of deterioration, but on several of the coarse-textured bricks there was slight surface crumbling. Examination of fractures showed fine cracks or crizzles in the matrix, particularly in the coarse textured bricks. Rough spalling tests were made by alternately slowly heating the bricks to 1,350°C. ; upon subsequently placing them on a cold iron plate, a much increased spalling tendency in the unprotected bricks was indicated. Chemical analyses of the stored bricks indicated no appreciable change in chemical composition in any of the batches. These observations emphasize the importance of adequately protecting silica bricks during storage. In order to investigate further this loss of strength, a number of briquettes were made from selected Totley ganister bonded with 2 per cent. of lime. The grading of the batches was as follows : *A* giving coarse-textured and *B* fine-textured briquettes.

	A	*B*
Passing 5 mesh but retained on 10 mesh	20%	10% by weight
,, 10 ,, ,, ,, ,, 20 ,,	17%	17% ,, ,,
,, 20 ,, ,, ,, ,, 90 ,,	20%	20% ,, ,,
,, 90 ,, ,, ,, ,, 120 ,,	25%	20% ,, ,,
Through 120 mesh	18%	33% ,, ,,

The average chemical analysis of the burned briquettes was :—

Silica	95·71%
Alumina	0·84
Iron Oxide	0·51
Titanium Oxide	0·22
Lime	2·04
Magnesia	0·16
Alkalies (as K_2O)	0·41
	99·89

The approximate size of the burned briquettes was 120 mm. × 22 mm. × 15 mm., and the weight 90 grammes. Batches of the briquettes were burned in a gas-fired laboratory furnace at 1,300°C., 1,400°C. and 1,500°C. Briquettes of each grade and each burning were then treated:

(*a*) By boiling in distilled water for 6 hours, the water being then evaporated to dryness in a platinum basin and the residue weighed and analysed. (Blank boilings, etc., were conducted in similar vessels as a check).

(*b*) By soaking for 1 week in cold distilled water; the water being then evaporated and the residue weighed and analysed.

(*c*) By supporting horizontally (the supports being under the extreme ends of the briquettes) in a glass vessel with free circulation of air, but protected from dust, and spraying to saturation with distilled water twice daily for 40 days. The drainage from the briquettes was evaporated, weighed, and analysed.

(*d*) The mechanical strength of the treated and untreated briquettes was compared by compression on edge in a Brinell machine.

The following are the results of these tests :—

A. Coarse texture briquettes burned at 1,300°C.
Powder density 2·49. Cold crushing strength 600 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·025	·018	·004	·003	500
Soaked *b* ..	·024	·016	·004	·004	500
Sprayed *c* ..	·018	·012	·003	·003	400

B. Fine Texture briquettes burned at 1,300°C.
Powder density 2·48. Cold crushing strength 650 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·033	·022	·004	·006	500
Soaked *b* ..	·029	·022	·002	·005	500
Sprayed *c* ..	·022	·016	·002	·004	450

A. Briquettes burned at 1,400°C.
Powder density 2·42. Cold crushing strength 650 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·021	·009	·055	·006	500
Soaked *b* ..	·012	·006	·002	·004	480
Sprayed *c* ..	·012	·007	·002	·003	450

B. Briquettes burned at 1,400°C.
Powder density 2·41. Cold crushing strength 700 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·025	·012	·006	·007	550
Soaked *b* ..	·016	·009	·002	·005	550
Sprayed *c* ..	·010	·005	·002	·003	450

A. Briquettes burned at 1,500°C.
Powder density 2·35. Cold crushing strength 700 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·009	·005	·002	·002	600
Soaked *b* ..	·007	·005	nil	·002	650
Sprayed *c* ..	·007	·005	nil	·002	550

B. Briquettes burned at 1,500°C.
Powder density 2·33. Cold crushing strength 750 lb. per sq. in.

Treatment	Wt. in grammes of dissolved material.				Cold crushing str. in lb. per sq. in.
	Total	CaO	Alkalies	Al_2O_3	
Boiled *a* ..	·011	·007	·002	·002	600
Soaked *b* ..	·008	·005	nil	·003	600
Sprayed *c* ..	·005	·004	nil	·001	550

The separation of the dissolved material into CaO, alkalies and Al_2O_3 is approximate; the Al_2O_3 contains a little silica and iron oxide.

There are definite indications that the loss in strength of silica bricks exposed to weather is in part due to a slight degradation of the bond by hydration and solution in water, as well as to the physical effect of frequent wetting and drying.

In these tests there is little or no distinction in the behaviour of the coarse and fine textured briquettes, but in both cases the briquettes burned at higher temperatures were more resistant to the water attack. The loss in strength was in all cases more marked with the long exposure to moisture in test *c*. This test is an approximation to the storing of bricks, without protection, in the open, and further emphasises the need for suitable protection of silica bricks during storage.

I am indebted to Mr. P. M. Robinson, M.Met., for assistance in carrying out the experimental work and making observations.

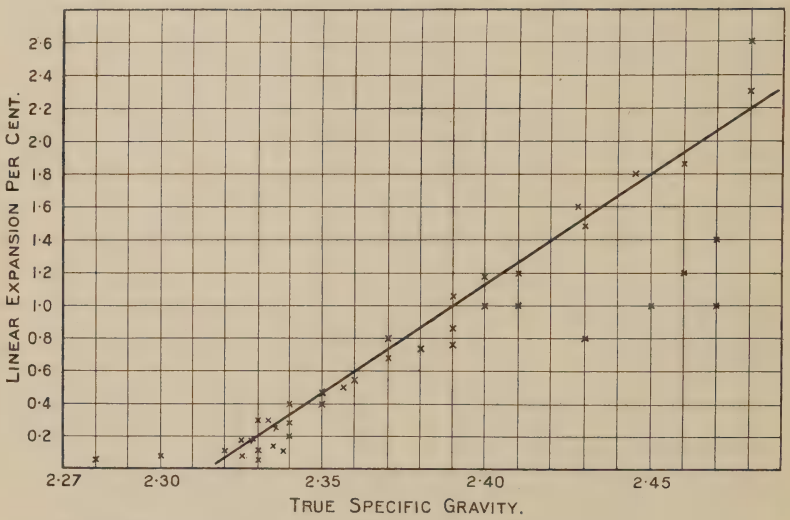
Department of Refractory Materials,
University of Sheffield.

VIII.—The True Specific Gravity and After-expansion of Lime-bonded Silica Bricks.

By W. J. Rees, B.Sc. (Tech.), F.I.C.

In connection with an investigation into the factors affecting the durability of silica bricks, observations have been made of the connection between the true specific gravity (or powder density) and the after-expansion of the bricks tested. The data for 40 bricks which have been examined are given in the graph and table of analyses appended :

The bricks are from North and South Wales, the Sheffield District, North of England, Scotland and France.



The following points are to be noted :—

(*a*) That for bricks of lime content between 1 and 3 per cent. there is a sufficiently close relation for practical purposes between the true specific gravity (or powder density) and the degree or extent of quartz conversion.

(*b*) That for bricks of fine and medium texture there is a close relation between the true specific gravity and the after-expansion as determined by the standard after-expansion test. For works purposes a rapid determination of the powder density of such bricks gives a definite indication of the permanent volume change which is likely to occur during their use.

TABLE OF ANALYSES.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Silica	95·40	95·47	94·07	95·15	94·67	94·57	92·73	95·62	95·10	95·40	95·19	95·03	95·87	95·16	93·02	92·59	95·33	96·73	95·06	94·76
Titanic Oxide ..	0·41	0·27	0·19	0·27	0·16	0·15	0·29	0·16	0·34	0·26	0·18	0·14	0·18	0·31	0·38	0·41	0·14	0·18	0·29	0·21
Lime	1·84	1·58	2·86	1·81	1·94	2·21	3·28	1·51	1·59	1·61	1·96	1·88	2·04	1·71	1·84	1·92	1·47	1·58	1·86	1·98
Magnesia	0·16	0·12	0·31	0·21	0·19	0·17	0·31	0·18	0·09	0·12	0·16	0·21	0·18	0·21	0·31	0·46	0·19	0·23	0·19	0·21
Alumina	0·74	1·06	1·02	1·21	2·18	1·84	1·71	1·02	0·91	0·88	1·02	1·14	0·71	1·06	2·14	2·28	0·91	1·01	0·91	0·90
Ferric Oxide	6·81	0·74	0·81	0·91	0·41	0·39	0·81	0·74	1·02	0·94	0·81	0·91	0·51	0·81	1·06	1·12	1·03	1·18	0·92	1·01
Alkalies (as K_2O) ..	0·51	0·61	0·51	0·36	0·57	0·61	0·81	0·61	0·71	0·61	0·58	0·71	0·49	0·54	1·02	0·96	0·51	0·61	0·71	0·74
Loss on ignition ..	0·07	0·06	0·11	0·04	0·06	0·04	0·12	9·04	0·08	0·08	0·06	0·04	0·04	0·06	0·14	0·14	0·06	0·06	0·08	0·09
Total	99·94	99·91	99·88	99·96	100·18	99·98	100·06	99·88	99·84	99·90	99·96	100·06	100·02	99·86	99·91	99·88	99·91	99·98	100·02	99·90
True Sp. Gr. ..	2·32	2·32	2·30	2·32	2·33	2·33	2·28	2·33	2·33	2·33	2·33	2·33	2·34	2·34	2·34	2·34	2·35	2·35	2·36	2·36
Apparent Sp. Gr. ..	1·71	1·74	1·64	1·65	1·61	1·61	1·54	1·68	1·71	1·74	1·78	1·62	1·63	1·71	1·68	1·76	1·78	1·71	1·70	1·71
Texture	F	M	F	M	F	M	F	M	M	M	F	M	M	F	M	M	F	M	M	C
Porosity per cent.	26·2	25·0	28·7	28·8	30·8	30·8	32·4	28·0	26·6	25·2	23·6	30·5	30·3	26·9	28·2	24·8	24·2	27·5	28·0	27·5
Linear After-Expansion per cent.	0·10	0·08	0·08	0·18	0·20	0·06	0·06	0·11	0·30	0·32	0·16	0·22	0·40	0·20	0·30	0·10	0·40	0·48	0·50	0·56

F—Fine Texture.
M—Medium Texture.
C—Coarse Texture.

TABLE OF ANALYSES—Continued.

	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Silica	95·45	94·39	95·50	95·97	94·87	94·76	94·59	95·56	94·62	94·48	94·29	95·24	96·46	94·65	94·97	95·05	95·18	94·70	95·72	93·33
Titanic Oxide ..	0·19	0·22	0·19	0·09	0·21	0·19	0·14	0·21	0·17	0·27	0·16	0·13	0·11	0·18	0·29	0·21	0·39	0·19	0·09	0·24
Lime	2·01	1·81	1·71	1·64	1·12	2·02	1·81	1·42	1·92	1·86	1·78	1·80	1·64	0·71	1·81	1·86	1·84	2 04	1·71	1·69
Magnesia	0·19	0·31	0·29	0·14	0·21	0·23	0·17	0·12	0·18	0·17	0·17	0·20	0·21	0·18	0·19	0·18	0·16	0·21	0·14	0·21
Alumina	0·71	1·84	1·02	0·91	1·94	1·08	1·16	0·86	0·91	1·21	1·46	1·02	0·64	1·04	1·12	1·08	0·76	0·91	0·86	1·86
Ferric Oxide	0·66	0·71	0·58	0·61	0·81	0·88	1·02	0·74	1·14	1·04	1·31	0·86	0·61	2·36	0·91	0·71	0·11	1·21	0·81	1·32
Alkalies (as K_2O) ..	0·71	0·41	0·49	0·51	0·86	0·61	0·81	0·91	0·71	0·81	0·87	0·58	0·45	0·61	0·56	0·69	0·58	0·61	0·91	1·01
Loss on ignition ..	0·06	0·11	0·13	0·09	0·12	0·13	0·14	0·09	0·16	0·14	0·12	0·09	0·09	0·18	0·09	0·18	0·09	0·09	0·10	0·21
Total	99·98	99·80	99·91	99·96	100·14	99·90	99·84	99·91	99·81	99·98	100·16	99·92	100·21	99·91	99·94	99·96	99·91	99·96	100·14	99·87
True Sp. Gr. ..	2·37	2·37	2·38	2·39	2·39	2·39	2·40	2·40	2·41	2·41	2·43	2·43	2·43	2·45	2·45	2·46	2·47	2·47	2·48	2·48
Apparent Sp. Gr. ..	1·69	1·69	1·75	1·74	1·71	1·69	1·61	1·75	1·74	1·66	1·81	1·78	1·75	1·68	1·76	1·68	1·81	1·76	1·84	1·80
Texture	F	C	M	M	M	C	C	M	C	M	C	C	M	F	C	F	C	C	C	M
Porosity per cent. ..	28·7	28·7	26·5	27·2	28·4	29·2	32·9	27·1	27·8	31·1	25·6	26·7	28·0	31·4	28·1	31·6	26·7	28·7	25·8	27·4
Linear After-Expansion per cent.	0·68	0·80	0·74	0·78	0·86	1·08	1·00	1·18	1·00	1·10	0·80	1·48	1·60	1·80	1·00	1·84	1·00	1·40	2·30	2·60

F—Fine Texture
M—Medium Texture.
C—Coarse Texture.

(*c*) That for the raw materials which are in use in this country for the making of lime-bonded silica bricks, the grading of the raw material has a greater influence on the rate of quartz conversion than variations in the source or type of the raw material itself.

(*d*) That for coarse-textured bricks containing large fragments of raw material (*i.e.*, $\frac{1}{4}$-inch, and above in diameter) there is not a close relationship between the true specific gravity and the after-expansion. This is probably due to the slower rate of inversion of the coarse fragments and their less intimate association with the lime in the matrix of the brick. It suggests the possibility that, for coarse textured bricks, the time of heating in the standard after-expansion test is insufficient. In the case of bricks Nos. 37 and 38, doubling the period of heating at 1,410°C. increased the after-expansion and brought it into relationship with the true specific gravity of the brick.

IX.—A Rapid Method for the Determination of True (or Powder) Specific Gravity.

By W. Hugill, B.Met., and W. J. Rees, B.Sc. (Tech.), F.I.C.

In view of the large number of determinations of powder density which will be necessary in connection with the research on silica bricks and grog bricks, we decided to make experiments with a view to devising a less laborious method than the usual one by pycnometer.

In testing the specific gravity of Portland cement a flask is used having a bulb and graduations on its neck. A definite volume of liquid is placed in the flask and a weighed quantity of cement is then gradually added. The volume of the cement is measured by the rise of the liquid into the graduated neck of the flask. A calculation then gives the specific gravity.

The experiments showed that, although the type and size of flask used in cement testing was not satisfactory for crushed bricks, the general method would be likely to give sufficiently accurate results.

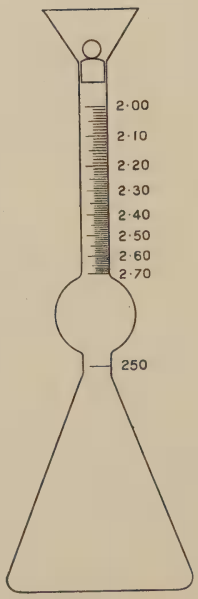


Fig. 1.

A flask was then made as illustrated in Fig. 1. The neck is graduated in specific gravities from 2·00 to 2·70, so that the specific gravity may be read off directly without calculation. The method of using it is as follows :—

Liquid is poured into the flask up to the 250 c.c. mark ; exactly 100 gms. of dry powdered brick is then gradually dropped into the flask. The liquid rises and after standing for 2 minutes, so that any air bubbles may rise, the level of the liquid is read on the graduated neck of the flask.

In view of the slight solubility of the lime bond of silica bricks in water and alcohol, and the comparatively high surface tension and viscosity factors of these two liquids, we decided to experiment with some of the liquid hydrocarbons which are readily obtainable in commercially pure condition.

The following are the physical properties of the liquids used as determined by us. As we were using (except in the case of water) commercially pure and not chemically pure liquids, it was not considered desirable to rely on data for pure liquids, and in fact for some of the liquids no data for surface tension and viscosity could be found so that actual determinations were essential.

TABLE A.

	B.Pt. °C	Density	Surface Tension dynes/cm	Viscosity at 13°C c.g.s.
Water	100	1·000	73·5	0·01189
Alcohol	78·3	0·794	22	0·01360
Benzene	80·2	0·879	29·7	0·00698
Toluene	111·0	0·867	27	0·00622
Xylene	140	0·864	27·3	0·00665
Tetrahydronaphthalene ..	200	0·979	35	0·02303

Powder density determinations of a brick were then made. One half of a silica brick was crushed to pass a 60 mesh sieve, and the other half to pass a 20 mesh sieve. The following results were obtained :—

TABLE B

	Benzene	Toluene	Xylene	Tetrahydro-naphthalene
Through 60 mesh (dried) ..	2·457	2·460	2·447	2·446
,, 20 ,, ,, ..		2·449	2·450	
,, 20 ,, (not dried) ..	2·441	2·440	2·446	

A determination of the powder density of this brick by the pycnometer method gave 2·458. Hence the results show that accuracy to plus or minus 1 in the second place of decimals could be expected from the method, provided that the crushed brick is dried. Of the liquids used, toluene and xylene appeared most satisfactory because of their low viscosity and surface tension. As xylene has a higher boiling point than toluene, it was decided to adopt it as the standard liquid for these tests.

The following experiments were then made in order to decide what degree of fineness was necessary to give sufficiently accurate results. Two bricks were each divided into four portions and the respective portions were crushed so as to pass a 10, 20, 30 and 40 I.M.M. mesh sieve. The results were as follows :—

TABLE C.

	Brick A.	Brick B.	By Pycnometer
Through 10 I.M.M. ..	2·432	2·375	Brick A 2·458
,, 20 ,, ..	2·445	2·385	Brick B 2·390
,, 30 ,, ..	2·450	2·385	
,, 40 ,, ..	2·450		

From this data it was considered that crushing the dry brick to pass a 30 mesh I.M.M. sieve gave sufficient accuracy in the powder density determination and further experiments have confirmed this.

The method used is therefore as follows :—

Not less than one quarter of a brick is crushed so that it will all pass through a 30 mesh sieve. The flask is then filled with xylene up to the 250 c.c. mark ; 100 gms. of the crushed brick are then weighed out in a counterpoised scoop and sprinkled into the flask. The flask is gently agitated to free any air-bubbles which may have been carried down. After standing for 2 minutes the powder density is read off directly from the level of the liquid in the graduated neck of the flask. A determination takes from 15 to 20 minutes, the greater part of this time being taken up in crushing the brick.

The results given in Table D below were taken on a sample of ganister after crushing and grading to the sizes shown :—

TABLE D

5-10	10-20	20-30	30-40	40-50	50-60	60-80	80-90	through 90
2·590	2·620	2·650	2·655	2·675	2·675	2·675	2·675	2·665

After the 5—10 grade had been crushed to pass a 30 mesh sieve its density was found to be 2·68 using the flask method.

X.—A Visit to the Osmosis Plant at Carlsbad.*

By S. R. Hind, B. Sc., A.R.C.S., A.I.C.

On April 13th, 1923, a visit was paid to the works of the Carlsbad Kaolin Electro-Osmosis Co., at Porchezau, Chodau, near Carlsbad, where I received every courtesy and assistance from the staff and, in particular, from Direktor W. Meyer.

GENERAL DESCRIPTION.

For the convenience of the general reader, the process has first of all been surveyed in general outline, and then, for those who are interested in the process from the chemical engineering point of view, the latter portion of the report is devoted to a more detailed survey. It is hoped that the author will be forgiven for the duplication necessitated by thus serving two masters. As far as possible, a discussion of the merits of the Osmosis Process has been avoided; this was dealt with in the larger report of which the present paper is only a part.

Mines, etc. The Electro-Osmosis Co. have two works close together, constructed of ferro-concrete. The raw material for both is obtained from two mines and a quarry in the neighbourhood. The overburden of gravel and surface clay is of a dark brown colour, and 10 to 15 feet thick; a further thickness of about 6 feet, immediately below, is rejected also in the open working, owing to the staining from the overburden. The deposits in some parts of the workings are of a low quality and darker colour, and are rejected (or avoided) as being unfit for the production of good china clay.

The raw material is brought to the surface, in the case of one mine, by a short shaft and suitable headgear, and in the other two workings by inclines provided with endless steel cable worked by electric power.

Each truck carries a weighed 600 kg. of raw material and runs to a discharging platform in the works where it is treated by a double set of toothed rolls, reducing it to a size of not more than 2 in., the greater part being much finer.

The raw material has to be mined by direct manual labour as it is too plastic for blasting and is said to wear away mechanical excavators extremely quickly on account of the very large proportion of coarse, sharp sand it contains. The plastic nature of the material is similarly stated to render useless the washing-out method em-

*Extracted from a report on "The Osmosis Process" and printed by permission of the British Refractories Research Association.

ployed in Cornwall. The process in use in the newer works will alone be described, as it differs only in detail from that in the first and older works. (See Fig. 1).

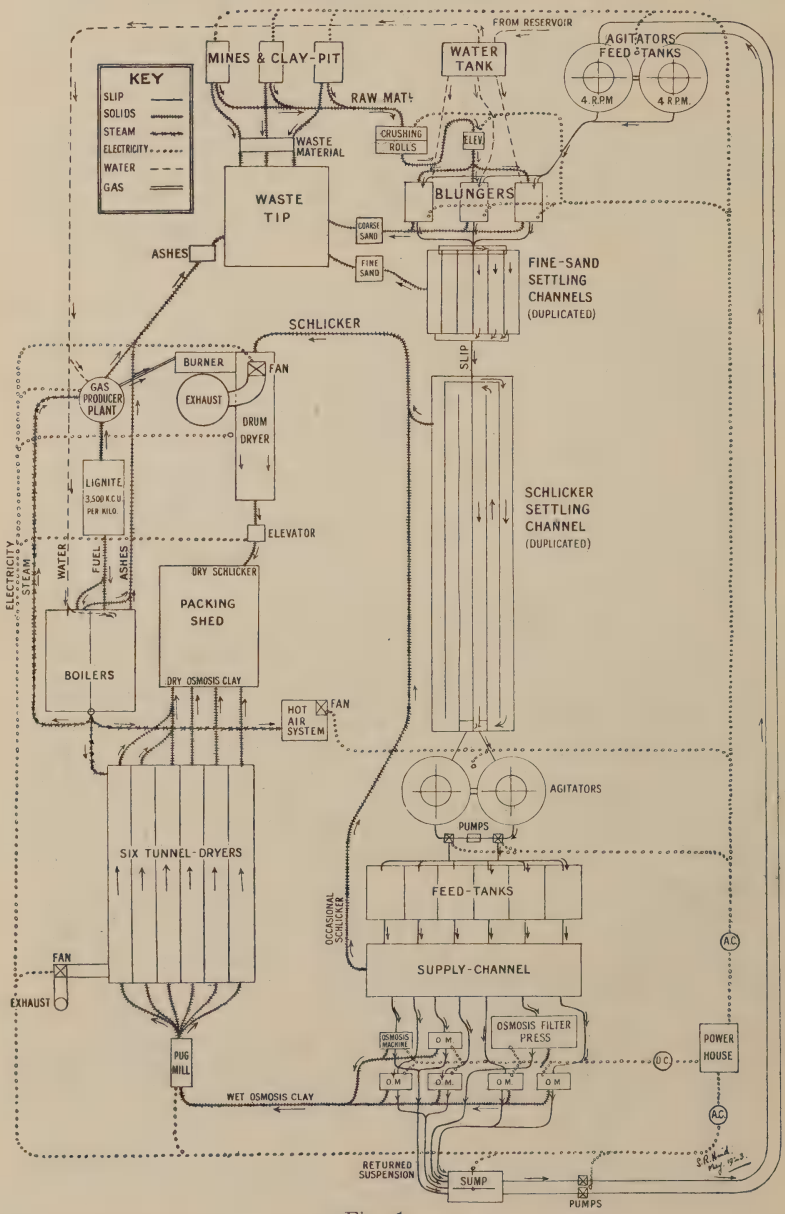


Fig. 1.
Flow-Diagram of Osmosis Plant, Chodau, New Works.

Blunging. The crushed earth from the rolls is elevated to a bin and thence fed into small tip-trucks for delivery to hoppers over the blungers (perhaps better described as washers). This hopper is provided with a slow-moving belt which regulates the delivery of the material into the blunger. The blunger (latest pattern), consists of four parallel, semi-cylindrical, open vessels, so arranged as to be equivalent to one long trough into which raw material and returned suspension enter at one end and a little water at the other. Sand is removed at this end also, and the suspension, re-inforced with the clay derived from the fresh raw material, finds its exit into a channel near to the hopper. The troughs are provided with helical agitators which slowly work the material towards the coarse-sand exit. The last two troughs are provided also with perforated buckets which lift the sand out of the suspension and tip it back again, the last of these delivering clean sand to a hopper whence it falls into a truck and is removed to the waste-tip. The coarse sand is thus separated from the clay in the blunger itself.

Settling System and Osmose Machines. The suspension or slip from the blungers still contains a considerable amount of finer sand and mica and this is next removed by directing the stream of slip into the fine-sand channels (Fig. 2). After these, the slip runs into a long channel where the coarser part of the china clay settles out (known as "Schlicker" and sold as paper-clay). From here it descends through a lawn, which retains small pieces of wood

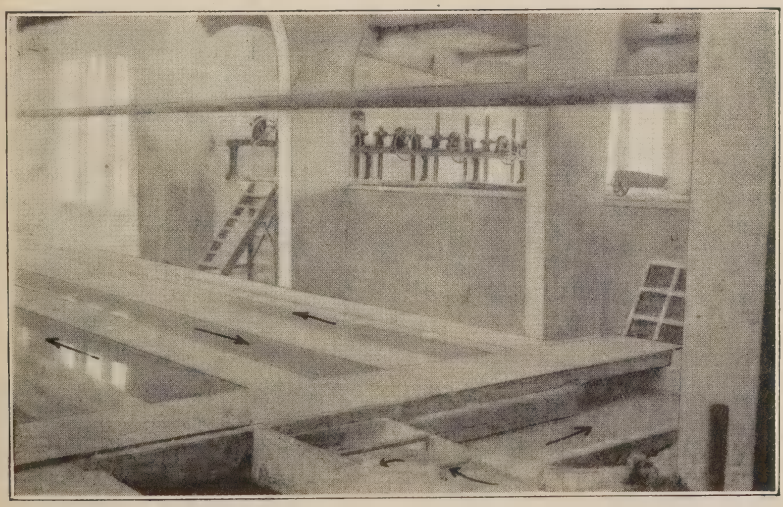


Fig. 2.
Showing part of Schlicker Channels and Fine Sand Channels.

and débris, into a pair of large storage tanks provided with agitators and connected together at their bases, from which it is pumped up to the feed-tanks of the osmosis machines, of which there are six. From these the slip, as required, is run into a common channel which supplies the six machines and an electro-osmosis filter-press, the purpose being to maintain the pressure of slip at the osmosis machines the same in all, with as little variation as possible. The method employed seems to be a very practical one for the purpose. The supply on the machines themselves is also controlled by a valve.

The waste, or returned slip after passing through the machines, gravitates through 4 in. copper pipes to a sump which is provided with a reciprocating agitator and from this it is pumped up by one of a pair of centrifugal pumps, provided for the purpose, into the feed tanks above the blungers. From here the suspension again proceeds through the cycle indicated.

Drying Fine Clay. The china clay from the machines ("Edelkaolin"), comes off in a fairly continuous sheet of 3 to 4 mm. ($\frac{1}{8}$") thickness and falls down a chute, the lower end of which consists of a cloth tube, into trucks on the floor below. These trucks supply a pug-mill close by, from which the clay is extruded in a hollow bar of the section shown in Fig. 3. This is cut up by wires into 3 sections at a time of about 3·5 cm. long. These sections are loaded on to dryer cars close by. The cars are about 1·50 m. high, and are provided with shelving accommodation calculated to hold as much wet clay as possible, leaving about 5 cm. air-spaces between the shelves as loaded and the pieces on the shelves.

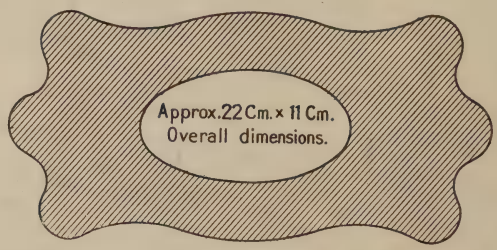


Fig. 3.

The cars when full are run into one of six dryers, which are parallel tunnels 30 m. long, where they travel forward a stage each time a new truck is run in, thus remaining in the dryer 22 hours in all. The drying-medium is hot air drawn by a fan over radiators heated by steam at $2\frac{1}{2}$ atmospheres pressure (37 lb. /sq. in.). The air leaving the radiators has a temperature of 65°., and is 20 to 24 per cent. saturated. It leaves the tunnel at a temperature of 36°, and is 90 to 95 per cent. saturated. The clay leaves the dryers with 10 to 12 per cent. of water. It is dumped on the

ground and loaded into sacks for removal by wagons in the adjoining covered siding.

Drying Schlicker. Periodically, the fine-sand and schlicker channels become filled up with material. This is not allowed to interfere with the continuity of the process. A duplicate set of channels is opened up and the filled ones are allowed to drain for a while, and then emptied. The fine sand is removed to the waste-tip. The schlicker, which is in a pasty form, rather troublesome to handle, is cut back vertically with spades, and loaded into buckets as shown in Fig. 4. These buckets are suspended from an overhead rail and trolley. When full they are run off to a hopper which feeds the dryer-drum. The front portion of this is shown in Fig. 5 and the arrows indicate, respectively :—

downwards	..	wet schlicker;
left to right	..	hot flue-gas;
right to left	..	moisture-laden air, through a fan;
upwards	..	indicates direction of rotation of drum.

The drying is by hot flue-gas in a brick channel. Air is introduced also through slide doors, and the temperature of the hot gases entering the dryer is thereby controlled. The hot gases travel down the core of the drum inside a pipe and then come back along the annular space between the pipe and the drum. In this way the hot air travels in a counter-current to the wet schlicker and effective drying is maintained. The schlicker comes out of the

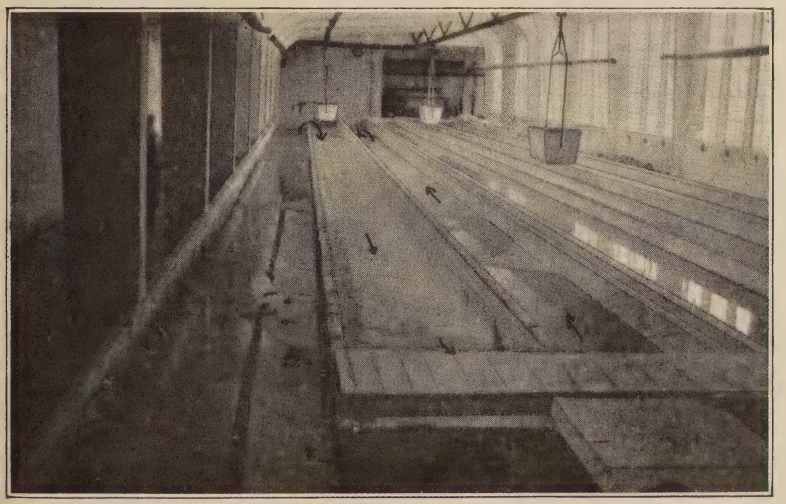


Fig. 4.
Schlicker Channels.

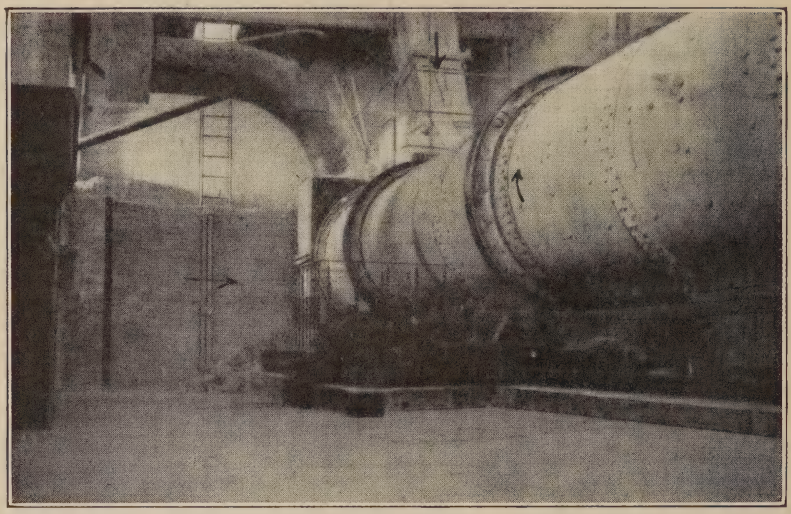


Fig. 5.
Schlicker Dryer Drum.

dryer hot, as rounded nodules, up to a size of about 2 cm. The exhaust conveys away a considerable quantity of dust and this is collected outside in a wide tower, from the top of which escapes the moisture-laden flue-gas. Periodically, this tower is opened, the dust dug out and added to the dried schlicker. It is said to be perfectly clean. At intervals of a week to a fortnight, the supply-channel above the osmosis-machines is cleaned out and the sediment obtained is added to the schlicker passing through the drying-drum. The producer gas is generated in a revolving bottom producer working on local lignite of calorific value 3,500 K.C.U. per kg. The gas is cleaned before transmitting to the burners, a considerable amount of tar being obtained.

Power, etc. Two boilers having each 220 sq. m. of heating surface, of the slow-fire type working on lignite of calorific value 3,500 K.C.U., generate steam at $2\frac{1}{2}$ atmospheres pressure.

The electric side of the power-plant generates 300 kilo-watts, partly steam-generated and partly received from an outside supply at 10,000 volts A.C. which is converted to 220 volts A.C. for power purposes. A part of this is also converted to direct current, the osmosis machines being supplied at 80 to 115 volts.

The works has a chemical laboratory for control purposes, mechanical and electrical fitting shops, and extensive stores. All the water used on the works is pumped up from a reservoir near by.

The works are very clean, the appearance being enhanced by the fact that the concrete was made with the waste sand from the

china clay. The resulting structure is almost dazzlingly white and glistens with mica particles. The machinery is of the latest type and is kept in excellent order.

DETAILED FIGURES RELATING TO THE PROCESS.

Fine-Sand Channels. These are in two sets of three channels each, one set being in use for settling, whilst the fine sand is being cleared out of the other. In each set the three channels are designed to be operated in parallel, though it appears to depend on the actual conditions at the moment as to whether one, two or three are in use.

The dimensions are :—1·68 m. deep, 1·46 m. wide, 13·00 m. long, thus giving a settling system approximately equivalent to one tank 4·38 m. wide, 1·68 m. deep and 13·00 m. long, when all these are in use together. The overflow is about 1·0 metres above the bottom, and sand is allowed to accumulate almost up to this level.

Schlicker Channels. These are also in two sets, one being in use while the other is being cleaned out. Each set consists of three parallel channels connected at their ends so as to be equivalent to one long channel 1·30 m. wide, 0·48 m. deep, and about 160 m. long. An adjustable weir controls the depth of the slip in the channels, so that this is maintained between 15 cm. and 25 cm. deep on top of the sediment. The aim is to maintain an average depth of 20 cm. When the channels are considered filled to a capacity, there is a 40 cm. depth of sediment, with 4 cm. of suspension above it, at the inlet end of the channel and 20 to 25 cm. depth of sediment, on top of which is 22 to 17 cm. of suspension, at the outlet end. The liquid surface, therefore, falls about 2 cm. in 160 metres.

The suspension runs over the weir into a wire-gauze which retains foreign particles, principally wood scraps from the mines, Through this gauze it passes into two agitators connected together at their bases. These are about 8 ft. diameter and 10 ft. deep. From these the slip is pumped (the pump and connections are duplicated) up to the six tanks above the osmose machines, as already described. These tanks have a capacity of 17 cu.m. each (total capacity 102 cu.m.).

The Osmosis Machines. (Fig. 6) The Osmosis machines are the same in principle as the small one at Stoke. There are six units. The drum consists of a homogeneous alloy of lead with 15 per cent. antimony and is covered with a layer of vulcanised rubber. The length of the drum is 1,432 mm., and the diameter 600 mm., the drum being complete with a 10 mm. layer of rubber. The lower half of the drum anode is surrounded by a grid cathode, the distance between them being 23 mm. from inner surface of grid to outer surface of rubber.

The drum makes one complete revolution in 3 min. 20 s.

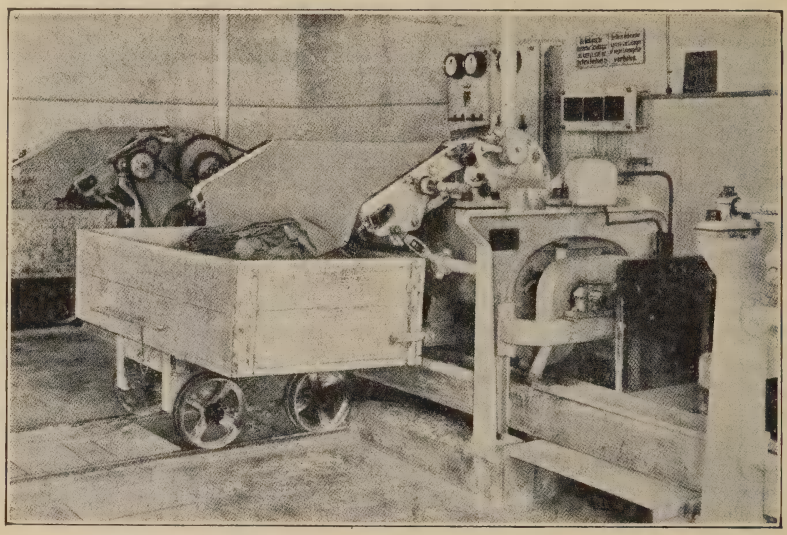


Fig. 6.
Electro-Osmosis Machine.

(18·0 revs. per hour). There are two stirrer-shafts parallel and in the same horizontal plane working in the slip below the drum. These revolve at 170 revs. per min.

The suspension, or slip, is fed into the lower part of the machine through a control-valve and overflows at the surface, finally falling by two pipes, one at the end of the machine, into a tray below the machine, whence it drains through copper pipes into a sump on the floor below. From here, as already described, it is pumped up to the storage above the blungers. (Sodium silicate, as required, is periodically added to the slip in this sump. The silicate is diluted with water before adding to the slip).

The machines each treat approximately 6 cu. m. of slip per hour. The handling of the clay from the machines has been described.

NUMERICAL DATA AND FLOW SHEET FOR THE PLANT.

Silicate of Soda. A solution of the monosilicate, Na_2SiO_3, is used, of specific gravity :—

36° Bé to 38° Bé., or 66·4° Tw. to 71·4° Tw., or S.G. 1·332 to 1·357

Ten litres of this solution are put into the sump for every 10,000 kg. raw material treated, though this is varied to suit immediate conditions (*e.g.* more would be used if the raw material were giving an unusually high proportion of kaolin.)

Current Consumption. On the osmosis machines (in normal running) this was observed to vary considerably, the average

figures being 103 volts and 171 amps. (D.C.), this giving a rate of current consumption per machine of 17·6 kilo-watts.

Average Yield of Clay from Raw Material (Dry weights).

Sand	64 per cent.
Schlicker	12 ,, ,,
Edelkaolin (Osmosis clay) ..	24 ,, ,,
	100 per cent.

The Edelkaolin varies from 23 per cent. to 26 per cent. with 24 per cent. as a good mean value.

Moisture in Materials.

	As first handled.	From dryers.
Raw Material	15 per cent.	—
Sand	5 to 10 ,, ,,	—
Schlicker	35 to 40 ,, ,,	3 to 5 per cent.
Edelkaolin	35 ,, ,,	10 to 12 ,, ,,

In-put of Raw Material. Trucks from the mines carry 600 kg. of raw material. The plant takes 15 trucks per hour, *i.e.*, 9,000 kg. per hour. A daily in-put of 176·5 tons corresponds best with the figures given to me, and also with my own observations; this is equivalent to 19·8 hours of full work per 24 hours.

Out-Put. The six machines give 40,000 kg. of clay in 24 hours, the weight being taken after drying to 10-12 per cent. moisture.

This will correspond to an annual output of about 10,000 tonnes dry china clay and 5,000 tonnes schlicker, or paper clay.

Densities of Suspensions. The following were given to me as normal working figures. My own observations are also given. They were taken after 14 hours' running subsequent to a stoppage, which may account for the difference from the "normal" figures.

TABLE 1.

Point of Observation.	Normal.			Observed.		
	°Bé.	Sp. Gr.		°Bé.	Sp. Gr.	
Exit of blunger	30	1·263		—	—	
Beginning of Schlicker-channels ..	28	1·241	·021	31½	1·280	·022
End of Schlicker-channels	26	1·220		29½	1·258	
Feed tank to Osmosis Machines ..	26	1·220	·020	29½	1·258	·022
Leaving Osmosis Machines ..	24	1·200		27½	1·236	

At the time of observation the suspension was entering the Osmosis machines at 15·5°, and leaving it at 18·6°. The clay was coming off the drum in a sheet 3 mm. thick and firm enough to handle with care. Two osmosis machines out of six, an osmosis filter-press and one washer out of three were in operation.

Check Test on Yield of Machines. From each of the two machines in operation a piece of the sheet of clay was taken midway between the centre and the edge of the drum and cut down to a rectangle of 25 cm. × 10 cm. These samples were carefully wrapped up in oiled silk and tested on my return to Stoke.

The following figures were thus obtained :—

Moisture in osmosis clay, as delivered from the machine	35·2	per cent.
Yield of clay in kg. dry weight per hour, per sq. m. of drum surface.. ..	74·5	,,
Thickness of sheet of wet clay from the machine, ignoring puffing-up by gas-bubbles	3·2 mm. or $\frac{1}{8}$ ins.	

This rate of output for six machines working 24 hours continuously would give :—

Dry weight	29·0	tonnes.
As from dryer, 11 per cent. moisture ..	32·6	,,
As from machine, 35 per cent. moisture	44·6	,,

The above yield would, therefore, appear to be low on account of abnormal conditions incident to starting up the plant. This is curious, however, as the measurements taken showed the suspension to be of a higher density than normal, and our own experience has always shown that, other things being equal, the greater the density of the slip, the greater will be the yield.

Consumption of Electricity (*Direct current for Electro-Endosmose*). The machines tested gave 201 kg. per hour each of dry clay with a mean power-consumption of 17·6 kilowatts, *i.e.*, at a rate of 0·0876 kilowatt-hour per kg. of dry clay or 87·6 units per tonne of dry clay. (This is 7s. 3½d. per ton of 2,240 lbs. at the English price of 1d., which is about twice the cost at the works in question.)

Capacities of Settling-Channels. It is estimated from the data that the fine-sand settling system (3 channels in parallel), would contain 59 tonnes dry weight filled to normal capacity. The schlicker-channel would, similarly, also hold about 59 tonnes dry weight of material, which, according to the flow-sheet hereafter, would take about 3 days to accumulate. There would then be a further 3 days in which to clean it out.

Normal Flow-Sheet. These figures relate to 24 hours' continuous operation in the new works.

TABLE II.

Material.		Weight in tonnes (1 tonne=1,000 kg.)
Raw material consumed ..	Moisture 15 per cent.	176·5
Dry material therein ..		150·0
Dry sand produced ..	64 per cent.	96·0
Dry schlicker produced ..	12 ,, ,,	18·0
Dry Edelkaolin produced (Osmosis clay)	24 ,, ,,	36·0
Water-Consumption. Removed with :—		
Sand	7·5 per cent. on wet wt.	7·78
Schlicker ..	37·5 ,, ,, ,,	10·76
Edelkaolin ..	35·0 ,, ,, ,,	19·38
Total water removed		37·92
Water added as moisture in raw material		26·48
*Water added daily in blungers		11·44

*The amount of water evaporated daily from the surface of the suspension in the channels and tanks may be considerable and will have to be allowed for here.

Calculation of Volume of Slip entering Osmose Machines. The fall in specific gravity of the suspension in passing through the Osmosis machines is 0·020 on 1·220, *i.e.*, $\frac{20 \times 100}{220}$ per cent.=9·1 per cent. only of the suspended material is removed in passing through the machines, the rest being returned for re-blunging, etc. The quantity of fine clay in suspension passing into the six Osmosis machines in 24 hours will, therefore, be of the order of 11×36 tonnes=396 tonnes dry weight.

The quantity of dry material in a cubic metre of suspension given by the formula

$$D = \frac{(A-1).\ B}{B-1} \text{ tonnes}$$

where D=weight of dry material, A=specific gravity of the suspension, and B=specific gravity of the dry material, which is taken as 2·60 for this material.

From this 1 cu. m. of suspension contains 0·3575 tonne dry clay, and, therefore, 396 tonnes are carried by $\frac{396}{0{\cdot}3575}$ cu.m. of slip, = 1,110 cu.m. of slip, and each of the Osmosis machines takes $\frac{1110}{24 \times 6}$ cu.m. per hour=7·7 cu.m. of suspension per hour.

A calculation based on the output actually tested, as described above, gives 5·6 cu.m. of suspension per hour for each machine.

These figures, therefore, support the previous one, of 6 cu.m. per hour.

Velocities of Flow in Settling Channels. On the basis of 6 cu.m. per hour per machine the channels will deliver approximately 36 cb.m. per hour, ignoring the comparatively small quantity of material which accumulates as sediment.

In the Schlicker-Channel:

Cross-sectional area of stream $=(0{\cdot}20\times1{\cdot}30)$ sq. m. $=0{\cdot}26$ sq.m.

$$\text{Therefore, velocity of stream} = \frac{36}{0{\cdot}26\times60}\text{ m. per minute.}$$
$$=2{\cdot}3\text{ m. per min.}$$

And the slip takes $\frac{160}{2{\cdot}3}$, or approximately 70 minutes to traverse the channel. This was checked at Stoke by the time required to sediment a sample of the same material at the same slop weight and depth, the conclusion drawn from the experiment being that the time required would be between 70 and 80 minutes.

It does not appear to be of any practical value to calculate similar figures for the fine-sand channels, as the material is so coarse as to settle through a metre depth of suspension almost completely in a few seconds. (It is nearly all retained in a 100's lawn). Also the suspension falls about half a metre, in a very rapid stream, into the channels and this must result in an agitation of the liquid sufficient largely to prevent settling of fine material. The obvious point about these tanks is that they must be large enough to accumulate a very considerable amount of sand in a comparatively short length of run.

Capacity for Storage. The four tanks, two being between the settling-channels and the Osmosis machine supply-tanks and two above the blungers, appeared to contain all the suspension during stoppages. Though they were not measured up, it is estimated that the four will hold about 120 cu.m. of suspension.

Drying Capacity of Two Types of Dryers. (Based on best figures available).

1. Drum-Drying for Schlicker. The Schlicker is dried to an average moisture of 4 per cent.

$\therefore$ Weight of moisture left in Schlicker daily $=\frac{4\times18}{96}=0{\cdot}75$ tonne.

Total moisture in wet Schlicker $=10{\cdot}76$ tonnes, whence moisture removed in dryer $=10{\cdot}01$ tonnes.

It follows, therefore, that the dryer evaporates 417 kg. of water per hour.

2. *Six Tunnels for China Clay.* The Edelkaolin is dried in these to an average moisture of 2 per cent.

Moisture left in china clay daily $= \frac{11 \times 36}{89}$ tonnes, $= 4 \cdot 45$ tonnes.

Total moisture in wet clay $= 19 \cdot 38$ tonnes.

Whence, moisture removed in 6 tunnels $= 14 \cdot 93$ tonnes.

This is equivalent to an evaporation of 104 kg. per hour in each tunnel-dryer.

Tests to Determine Purification Actually Attained in the Osmosis Machines.

A sample of kaolin from the Osmosis machine, and as delivered from the dryers, was submitted to analysis and a test for refractoriness. This was compared with a sample of clay prepared from the raw material used at Chodau, by sedimentation of the impurities and recovery of the whole of the remaining suspended material.

The raw material was worked up with water and deflocculated with sodium silicate, washed through lawns up to 200's mesh (to take out coarse grit) and allowed to settle at a depth of 24·5 cm. until the slop weight decreased from 24·1 oz. per pint to 22·8 oz. per pint. The slip was then gently evaporated until dry. The results of the tests on the two products are given below :—

Table I.

Sample.	Osmosed product.	Settled only.
Refractoriness : Cone ..	36	36
Temperature of squatting ..	1,790°C.	1,790°C.
Chemical Analysis.	%	%
SiO_2	45·13	45·66
TiO_2	0·51	less than 0·01
Al_2O_3	37·89	37·12
Fe_2O_3	0·94	0·87
MgO	0·29	less than 0·01
CaO	0·48	0·46
K_2O	0·78	0·88
Na_2O	0·58	0·74
Loss when heated above 109°C. ..	13·52	13·86
Rational Analysis (Calculated)	%	%
Clay	90·2	88·5
Felspathic (or micaceous) matter	8·1	9·7
Quartz	Nil	Nil
Iron Oxide (Fe_2O_3) ..	0 9	0·9
Lime (CaO)	0·5	0·5

One is, therefore, led to believe that, for all practical purposes, the whole of the purification of the material takes place in the preliminary settling, the Osmosis machine being simply a convenient means of removing the clay from suspension.

XI.—The Influence of Oxidising and Reducing Atmospheres on Refractory Materials.*

PART I.—Experiments with a Cone-mixture containing added amounts of a Ferruginous Material.

By A. E. J. Vickers, B.Sc., and L. S. Theobald, B.Sc., A.R.C.S.

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Introduction.

The importance of the part played by the atmosphere, be it oxidising or reducing, in which refractory materials are enveloped, has long been realised, and in many instances, the effects produced have been noted, mostly in a general way.

Several cases have been reported of the disintegration of firebrick resulting from the action of reducing gases on the refractory materials in use. For example, T. Holgate[1] in 1905, drew attention to two cases of failure in the linings of blast furnaces, one described by J. Pattinson[2] and the other by F. Firmstone[3], whilst a third case is reported by L. P. Ross.[4]

In every instance, the disintegration of the linings is attributed to the deposition of carbon, resulting from the decomposition of carbon monoxide in the presence of the oxides of iron. The same explanation is put forward by O'Hara and Darby[5], as a conclusion drawn from their experiments concerned with the effect of carbon monoxide on refractory brick, with the object of explaining the disintegration which developed in the condenser of a zinc distillation apparatus.

The conditions of atmosphere play an important part in the pyrometric use of Seger cones, a fact which has been emphasised by many workers[6].

C. Loeser[7] compared the behaviour of Seger cones in oxidising and reducing atmospheres and noticed marked differences in the appearance of the residues which he obtained.

Bradshaw and Emery[6] examined the behaviour of cones in an atmosphere of coal gas and observed the formation, at the surface of the cone, of a thin, refractory shell of hard carbon which remained standing while the interior molten slag could be drained away.

Similar results were obtained with a few test pieces of fireclay

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1 T. Holgate, *Gas Lighting*, **91**, 170, 230, 1905.
1 J. Pattinson, *J. Iron, Steel Inst.*, 85, 1876.
2 F. Firmstone, *Trans. Amer. Inst. Min. Eng.*, **34**, 427, 431, 1904.
3 L. P. Ross, *Iron Age*, **2**, 117, 1920.
4 O'Hara and Darby, *J. Amer. Cer. Soc.*, **6**, 904, 1923.
5 J. W. Mellor, Trans. **17**, 93, 1917-18.
6 L. Bradshaw & W. Emery, Trans. **21**, 117, 1921-22, and following references.
7 C. Loeser in Loeser's *Ber. für Keramik*, **19**, 111, 1910.

brick treated under like conditions, and fireclay mixed with small amounts of ferruginous marl behaved in an analogous way.

In 1915, L. S. Marks[8], working in connection with the fusibility of coal ash, drew attention to differences as great as 390°C. which were obtained on the same samples of ash by independent laboratories. He, himself, was able to obtain similar discrepancies, which he attributed to the oxidising or reducing action of the furnace atmospheres in which the tests were made.

The question has been investigated more fully by Fieldner, Hall and Feild[9]. In their admirable work on the fusibility of coal ash and the determination of the softening temperature, they have made comparative tests in the six different furnaces used in their experiments, each furnace giving a different atmosphere. Their results show, in no indefinite way, that of all the factors—such as size and position of cone, fineness of particle and rate of heating—which influence the determination of the softening temperature of a given ash, atmosphere is by far the most important. Summing up, these investigators state that "the highest softening points were obtained in an atmosphere of air (platinum wire furnace) or in a strongly reducing atmosphere of carbon monoxide (Northrup furnace) which prevented the iron oxide from acting as a fluxing agent by reducing it to metallic iron before the softening of the ash began. The lowest softening temperatures were obtained in those atmospheres of mixed gases in which reduction of ferric oxide proceeded mainly to ferrous oxide.....The maximum variation in the softening temperatures due to different atmospheres ranged from 134° to 396°C."

The invariable presence of iron compounds in fireclay and the effects on colour, fusibility, etc., which are attributed to them, make it a matter of first importance to consider them in relation to various atmospheres, whether oxidising or reducing. J. W. Mellor[10] determined the softening temperatures of artificial mixtures of refractory material and ferruginous fuel ash. The introduction of up to 28% ferric oxide in the form of ash, was accompanied by a lowering of the softening temperature from 1,710°–1,160°C., and he cites this as an example of the sensitivity of ordinary fireclays to the presence of admixed iron compounds under reducing conditions. In this case, the reducing action was produced by the carbonaceous matter in the fuel ash.

R. Rieke[11] and G. Flach[12] also investigated the fusibility of mixtures of clay and iron compounds.

Fieldner, Hall and Feild,[13] likewise support the opinion that lower softening temperatures may be expected if the conditions of atmosphere are such as to reduce the iron, not to the metallic,

8 L. S. Marks, *J. Amer. Soc. Mech. Eng.*, **37**, 205, 1915.
9 A. C. Fieldner, A. E. Hall and A. L. Feild. "The Fusibility of Coal Ash and the Determination of the Softening Temperature." *U.S. Bur. Mines.* Bull., No. **129**, 37-43, 1918.
10 J. W. Mellor, TRANS. **13**, 12, 1913-14.
11 R. Rieke, *Sprech.*, **43**, 198, 214, 229, 1910.
12 G. Flach, *Sprech.*, **44**, 171, 187, 205, 219, 626, 1911.
13 loc.cit.

but to the ferrous state.

In view of the important rôle thus played by iron compounds, it has been decided, in the present work, to add known amounts of ferruginous material to the system under investigation, and to examine the softening temperatures of the various mixtures in separate atmospheres of the more common gases, viz., nitrogen, air, oxygen, hydrogen, carbon and sulphur dioxides, and water vapour.

The results now presented have been obtained with Thivier's Earth[14] as the iron-bearing constituent. The addition of iron in other forms will be dealt with in subsequent papers.

MATERIALS OF EXPERIMENT.

The series of experiments reported was made on a supply of an ordinary cone mixture substance and Thivier's Earth added in known amounts. This cone mixture was chosen as the basic material of these investigations because of its comparative purity, its low iron content and because of the fact that its normal softening temperature, viz., 1,410°C. carries the temperature range of the experiments into the region of practical working conditions such as are met with in the normal use of a refractory material. Thivier's Earth was adopted, on the suggestion of Dr. A. Scott, as a convenient source of known amounts of iron for addition to the cone mixture*. Analyses of the mixture and of the Thivier's Earth are:

TABLE I.

ANALYSES OF MATERIALS USED. (H. Edwards).

Cone Mixture.

SiO_2	72·86%
TiO_2	0·04
Al_2O_3	17·04
Fe_2O_3	0·35
CaO	1·32
MgO	0·15
K_2O	4·81
Na_2O	1·11
Loss	2·62
	100·30

Rational Analysis.

Clay	26·29	per cent.
Spar	35·06	,,
Quartz	37·00	,,
Ferric oxide, etc.	0·35	,,
Lime	1·30	,,

Thivier's Earth.

SiO_2	83·18%
TiO_2	—
Al_2O_3	2·30
Fe_2O_3	9·87
FeO	0·33
MnO	0·04
CaO	0·83
MgO	0·12
K_2O	0·58
Na_2O	0·22
Loss	2·82
	100·29

Rational Analysis.

Clay	3·67	per cent.
Spar	4·90	,,
Quartz	80·11	,,
Ferric oxide, etc.	10·47	,,
Lime	0·85	,,

14 *Note on so-called "Thivier's Earth."* This material is the same as that supplied to and used in the ceramic industry under the name "Thivier's Earth." The only reference to this earth which has been found in the literature describes a material quite different in chemical composition and properties to that which has been used in these experiments (see anal. given below). Vogt et Laverard. *Argiles et Céramique: Mémoires de la Société d'encouragement pour l'industrie National.* p. 167, Paris, 1906.

* The cone mixture was known to give constant softening temperatures under given conditions; the Thivier's Earth was graded and that portion selected which passed through an 80's, but remained on a 100's lawn.

A series of cones containing 5, 10, 15, 20 and 25 per cent. of Thivier's Earth was prepared (reference numbers A1, A2, A3, A4 and A5 respectively). Their content of ferric and ferrous iron is given as percentages in Table II. The cones were moulded in the shape of a solid triangular pyramid of base 1·8 cms. and height 6·4 cms.

TABLE II.

Cone	A1.	A2.	A3.	A4.	A5.
Fe''	0·0128	0·0262	0·0396	0·0530	0·0664
Fe'''	0·3510	0·7080	1·0830	1·4320	1·7530
Fe'' as FeO ..	0·0165	0·0324	0·0510	0·0682	0·0850
Fe''' as Fe_2O_3 ..	0·5010	1·0120	1·5470	2·0420	2·5020

The average ratio of ferrous to ferric iron in each cone is 1 : 27. The average ratio of FeO to Fe_2O_3 is 1 : 30.

The methods[15] which have been employed for the determination of iron are as follows :—

Ferrous Iron.

15 grams of the material are dried for 1 hour at a temperature of 105°C., and cooled in a desiccator. 5 grams of the material are then weighed out into a tared platinum crucible and broken up into coarse lumps. 12 ccs. of sulphuric acid (1 vol. concentrated acid to 1 vol. of water) are now added, followed by 10 ccs. of hydrofluoric acid. The crucible and its contents are warmed for 10 minutes over a small luminous flame, and then plunged into 400 ccs. of distilled water, which has been boiled until quite free from air, and which contains 10 grams of pure, precipitated silicic acid and from 20 to 25 grms of pure potassium sulphate. The solution is titrated with $N/100$ potassium permanganate, until a pink coloration, lasting for one minute, is obtained.

Total Iron.

1 gram of the mixture is fused with sodium carbonate, to which a little potassium nitrate has been added (to oxidise ferrous iron to the ferric state), silica is separated by the usual method, and the iron-alumina precipitate brought down. This precipitate is re-dissolved and the iron content determined by reducing with stannous chloride, the excess of stannous chloride being removed by precipitation with mercuric chloride. Reinhardt's solution is added to sharpen the end-point and the solution is titrated with standard potassium permanganate as before.

APPARATUS.

The apparatus used in the investigation is a modified form

15 The estimation of ferrous iron, especially in such small amounts as the present is an operation of much uncertainty. (See *U.S.A. Geological Surv. Bull.*, No. 700, p. 189, et seq.) and the above figures, therefore, are given with reserve. Furthermore, carbon determinations on the Thivier's Earth showed the presence of possibly a small amount of free carbon therein (not greater than 0.1%) and this adds somewhat to the uncertainty of these figures.

of that described by Bradshaw and Emery.[6] The ordinary Hirsch refractory furnace has the usual supports and lifting gear removed. These are replaced by a device shown at H, Fig. 1, which consists of a cast iron vessel through which a continuous stream of water is made to flow. Passing through the vessel in a central position is a tube which serves to conduct the atmosphere which it is desired to use in the experiment, into the central chamber of the furnace.

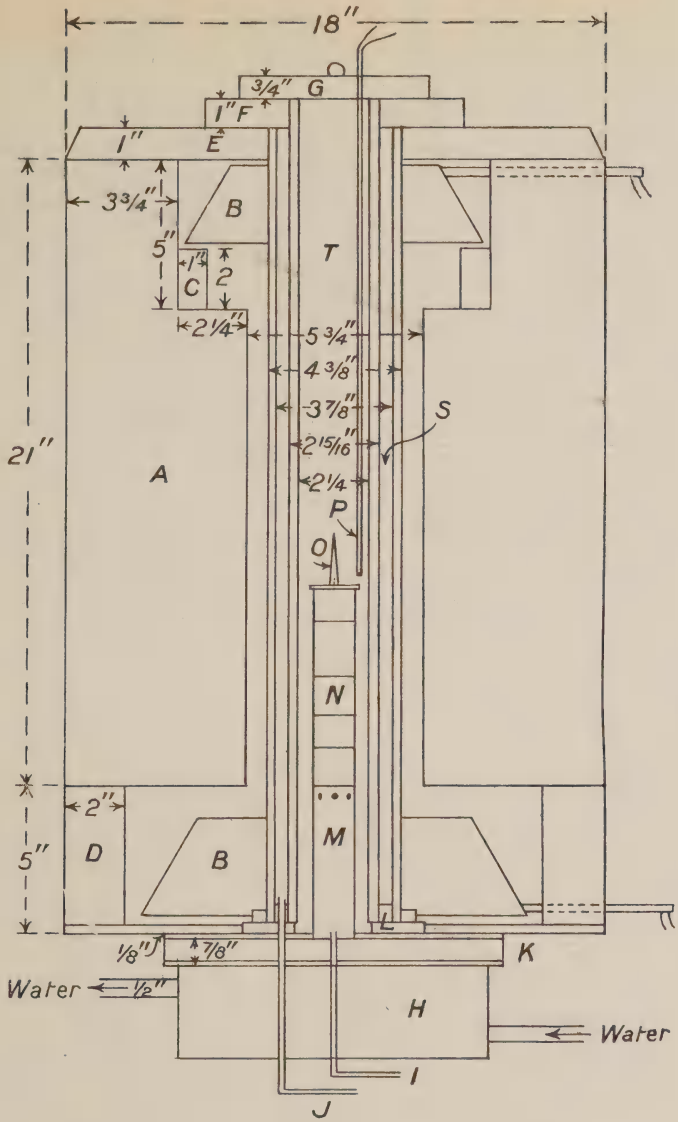
The tube, *J*, conducts a neutral gas (nitrogen) into the annular space, *S*, the function of which will be described later. The modifications in the furnace proper consist in replacing the usual central tube by two tubes arranged co-axially. These are held in position by a device shown in detail at *R*, where this device, in addition to maintaining the two tubes in position, prevents the leakage of gas from the annular space into the central chamber. The reason for the adoption of this arrangement of co-axial tubes is that at high temperatures a considerable evolution of carbon monoxide takes place at the surface of the central tube of a Hirsch furnace and if this gas were allowed to react with the substance of the material under test, the effects of the specific atmosphere might be masked. By sweeping out the annular space with a current of nitrogen, the danger of the diffusion of carbon monoxide into the inner tube is greatly lessened. The high temperatures required in the outer tube in order to reach the temperature desired in the inner, rendered impracticable the use of tubes of the ordinary materials. The tubes employed in these experiments were of clay-bonded, natural sillimanite and were prepared by Mr. W. Emery.

Method of Experiment.

The method of conducting an experiment consists in cementing the test piece to a fireclay support, passing a steady stream of nitrogen through the annular space, *S*, and a steady stream of the gas under investigation through the central tube, *T*, by means of the gas distributor *M*. In each run the rates of flow of the gases were kept, as nearly as possible, the same.

The furnace temperature is raised at 10°C. per minute, but this rate is retarded somewhat when within 150°C. of the expected softening point of the test piece. The rates of heating were controlled by the use of a thermocouple and recording galvanometer up to a temperature of 1,000°C. The final temperature at which the piece softened was measured by an optical pyrometer of the disappearing filament type focussed on the test piece itself. The pyrometer was checked against a standard platinum platinum-rhodium thermocouple under conditions similar to those which obtained in the experiment.

The temperature reading of the piece when it has bent half-way to the base is taken as the softening temperature for the purpose of this report.



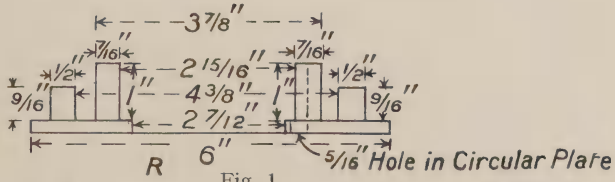


Fig. 1.

Hirsch Electric Furnace, modified for experimental research on Atmospheres.

A	Refractory lining for furnace.
B, *B*	Electrodes
C	Support for electrodes.
D	Support for furnace.
E, *F*, *G*	Covers for furnace, annular space and inner chamber.
H	Water-cooled gas inlet and support.
I, *J*	Inlets for gas and nitrogen.
K	Asbestos gas-tight joint.
L	Support for tubes.
M	Gas distributor.
N	Support for test-piece.
O	Test-piece.
P	Thermo-electric-pyrometer.
R	Detail of *L*.
S	Annular space.
T	Central chamber.

Each series of experiments was performed in duplicate and, in every case, the final temperatures for the softening point of each piece agreed to within a few degrees centigrade.

RESULTS.

The experimental results obtained with the various atmospheres will now be considered individually and in some detail. In this connection reference should be made to Fig. 2, which shows the points given in Table III. and obtained with the series A1, A2, etc., in the atmospheres of nitrogen, oxygen, air, carbon and sulphur dioxides, and hydrogen.

TABLE III.

SHOWING SOFTENING TEMPERATURES IN °C. IN VARIOUS ATMOSPHERES.

Atmosphere ..	N_2.	O_2.	Air.	SO_2.	CO_2.	H_2.
Cone mixture ..	1415°	1420°	1420°	1410°	1425°	1420°
A1 ..	1425°	1450°	1440°	1400°	1425°	1390°
A2 ..	1440°	1460°	1450°	1410°	1425°	1350°
A3 ..	1460°	1475°	1460°	1410°	1425°	1305°
A4 ..	1475°	1490°	1470°	1410°	1420°	1285°
A5 ..	1485°	1490°	1485°	1410°	1415°	1240°

Nitrogen.

Nitrogen being considered a neutral gas, determinations of softening temperatures were made in it in order to provide some sort of standard whereby the results obtained with other gases might be compared and interpreted.

The curve marked N_2 in Fig. 2 shows the results with this gas. Incidentally, it should be noted that the Thivier's Earth used has, by itself, an ordinary refractoriness in air of Cone 28 (1,630°C.). Its addition, therefore, would probably tend to increase that of the cone mixture, which, on testing, was found to bend over half-way, when a temperature of 1,415-20°C. was reached.

Inspection of the curves for nitrogen (Fig. 2) seems to support this by showing that the softening temperature increases regularly on passing from a mixture which contains 5 per cent. of Thivier's Earth (Series A1) to one containing 25 per cent. (Series A5).

The test pieces increased in size to a marked degree, and developed a pronounced vesicular structure, while the actual bending of a cone was comparatively slow.

Oxygen.

The influence of an atmosphere of oxygen is shown in the uppermost curve in Fig. 2. The most noteworthy point here is the marked increase in refractoriness which occurs more especially at the beginning of the curve, although the gradient generally is not so steep as in the case of nitrogen.

Air.

The behaviour of the cones in air is practically intermediate

between that developed in nitrogen and that developed in oxygen. This is what may be expected if the increased refractoriness in the series with oxygen is due, as it appears to be, to the oxidation of the ferrous iron present.

Swelling and the development of vesicular structure occurs in air as well as in nitrogen and in oxygen.

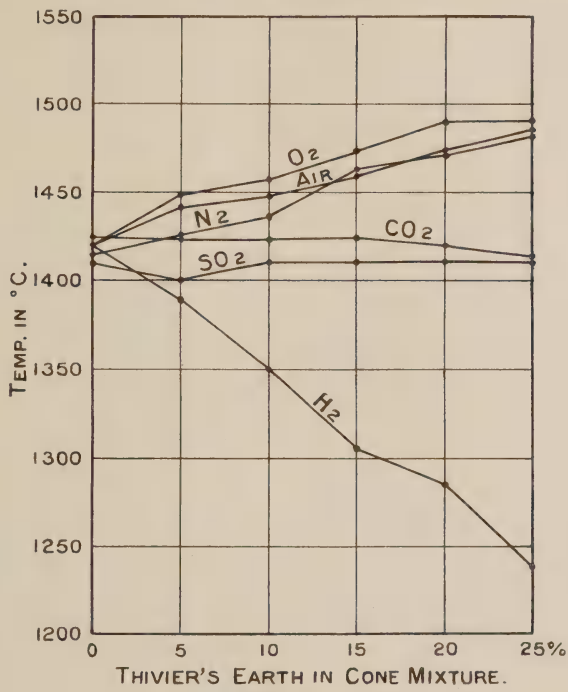


Fig. 2.

Curves showing the Effect of Different Atmospheres on a Cone Mixture containing added amounts of a Ferruginous Earth.

Sulphur Dioxide.

In an atmosphere of sulphur dioxide the same softening temperatures were obtained for the test pieces containing 10, 15, 20, and 25 percentages of Thivier's Earth. This is remarkable in so far as the tendency of the Thivier's Earth to enhance the refractoriness of the pieces is apparently just counterbalanced by the tendency of the sulphur dioxide, functioning as a reducing gas, to lower this value. The formation of a vesicular structure in this series is also peculiar. Mixtures containing 5 and 10 percentages of added earth do not show it, the cones having the same type of appearance as the pieces heated in a reducing atmosphere, but as the percentages of Thivier's Earth increase from 10 to 25, vesicular

structure develops and the cones gradually assume the character of the pieces fired in an oxidising atmosphere.

Carbon Dioxide.

In the series of mixtures heated in carbon dioxide, all the cones softened at practically the same temperature, resembling in this respect those in sulphur dioxide. There was, however, a tendency for the softening temperatures to become lower as the content of Thivier's Earth increased. This series of experiments, then, appears to show that carbon dioxide is functioning as a reducing gas under these conditions. The occurrence of a vesicular structure is again remarkable; it occurs with the lower percentages of added earth but not with the higher, a reversal of the condition of affairs which results with sulphur dioxide.

These two cases of sulphur and carbon dioxides are of peculiar interest and further investigations with pure iron oxides as the iron bearing constituent, are now being made.

Hydrogen.

Of all the results described, those obtained in an atmosphere of hydrogen prove to be by far the most decisive and the most striking. As will be seen from the curve for this gas (Fig. 2), a marked reducing action, judging by the softening temperatures, takes place. The refractoriness falls off at a rapid rate with increasing content of Thivier's Earth, so much so that in the case of mixture A5, which contains 25% earth (0·08% FeO and 2·5% Fe_2O_3), the softening temperature is some 250°C. lower than that at which a similar piece softens in oxygen, and 245°C. lower than in an atmosphere of nitrogen.

No increase in size or development of vesicular structure occurred, the edges of the softened cones remained quite sharp, and the pieces bent with a rapidity which was, comparatively speaking, great. In order to detect any metallic iron of appreciable size which may have been formed in the above experiments, cones from each series were immersed for two hours, with one surface freshly ground, in a dilute solution of copper sulphate. Under a magnification of 120 diameters, however, no particles of free iron, plated by copper, could be detected.

Colour of the Cones.

The colours of the test cones after heating in the various atmospheres and cooling in air, are worthy of note (Fig. 3), and for purposes of comparison a colour photograph is shown.

The pinkish colour developed by Cones A1 and A2 in oxygen offer a sharp contrast to the stone colours which are obtained with the corresponding cones in an atmosphere of nitrogen. In air, this is even more marked, the first two cones having a colour deeper even than the corresponding cones in oxygen.

The colours in hydrogen are remarkable in that they are the most pronounced and the most uniform obtained in any of the

Fig. 3.

series. In sulphur dioxide and carbon dioxide, there is a general lightening in tint when comparisons are made with the results in hydrogen.

In each series, there is a deepening of colour as the iron content in the cones increases.

For comparisons in size, the middle cones of the hydrogen series may be regarded as typical of the size of the cones before heating in the furnace.

SUMMARY.

(1). The effect of the various atmospheres on a cone mixture containing various percentages of a ferruginous earth, has been examined.*

(2) The softening temperatures of the pieces increased in oxygen and in air compared to the values obtained in nitrogen as standard.

(3). Sulphur dioxide and carbon dioxide appear to act as reducing gases under the conditions of experiment.

(4). Hydrogen acts strongly as a reducing gas, the softening temperature of the pieces with the highest content of iron being lowered some 250°C.

(5). The variations in colour with the different atmospheres have been noted.

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*The importance of the part played by various atmospheres in the use of refractory materials has been pointed out, and will also suggest itself in connection with their manufacture.

XII.—The Influence of Oxidizing and Reducing Atmospheres on Refractory Materials.†

PART 1 (continued). Experiments with a Cone Mixture containing added Amounts of a Ferruginous Material.

By A. E. J. Vickers, B.Sc. and L. S. Theobald, B.Sc., A.R.C.S.

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Introduction.

THE majority of published researches upon the influence of gases on refractory materials have been concerned with the effect of carbon monoxide upon such materials containing compounds of iron[1]. These researches have been confined to effects at comparatively low temperatures.

The action of carbon monoxide as the cause of the disintegration of a firebrick is of considerable importance in many industrial operations, such as in the zinc distillation industry[2], and in the running of a carburetted water gas plant, where much disintegration of the firebrick may be observed to take place in the carburetter and super-heater of a plant which is being operated for the manufacture of blue gas. The vessels in this case, being maintained at temperatures of from 400°C. to 550°C. in an atmosphere of carbon monoxide, provide optimum conditions[2] for the deposition of carbon* around any ferruginous material which may exist in the refractory material. Many investigations have been made with reference to the deposition of carbon within the material of the refractory linings of a blast furnace[3], the deposition in this case also being of the low temperature type.

Some attention has been paid to the effect which water vapour may have upon the melting point of a pure mineral. F. Guthrie[4] was one of the earliest investigators to call attention to the effects of the presence of water on melting points; he suggested, as an explanation of his work, that fusion should be considered as an extreme case of liquefaction by solution, and further, that solution and mixture are continuous with one another in some cases at temperatures which are not above the temperature of these bodies *per se*. A. Geikie[5] applies Guthrie's work in order to account for the presence of minerals of high melting point in rock structures which have clearly been formed by the crystallization of the components at comparatively low temperatures.

1 Literature quoted on page 86.
2 B. M. O'Hara and W. A. Darby, *J. Amer. Cer. Soc.*, **6**, 904-914, 1923.
3 Lowthian Bell, *J. Iron Steel Inst.*, **5**, 83, 1872.
J. Pattison, *J. Iron Steel Inst.*, **11**, 85, 1876.
C. E. Nesbitt and M. L. Bell, *Iron Trade*, **72**, 1803, 1923.
L. P. Ross, *Iron Age*, **2**, 117, 1920.
4 F. Guthrie, *Phil. Mag.*, **18**, 117, 1884.
5 A. Geikie, *Text Book of Geology*, Vol. **1**., 413, 1903.
* The authors in their experiments at elevated temperatures have not obtained any deposition of carbon. This result is in accord with those obtained by previous investigators.

The series of experiments described in the present paper is a continuation of those reported on p. 86 *et seq.* The authors have confined their investigations to the action of gases at high temperatures, that is, temperatures well over 1,000°C., to which refractory materials are subjected in general use. The apparatus and materials are the same as those used in the first series of experiments, the atmospheres under consideration being those of carbon monoxide and water vapour.

Preparation of Carbon Monoxide.

The carbon monoxide used in the experiments was prepared by allowing a steady stream of formic acid to fall into concentrated sulphuric acid, which was maintained at a temperature of 105°C. The gas was passed through a strong solution of potassium hydroxide in order to absorb any free formic acid, carbon dioxide and sulphur oxides, which might pass over ; it was then passed through an alkaline solution of pyrogallol in order to remove oxygen, and finally through sulphuric acid to dry it.

The water vapour was supplied by boiling water in an ordinary tin vessel, and was slightly superheated before passing into the furnace.

Results.

The results obtained are set out in Table I., and shown graphically in Fig. 1. Fig. 2 is a graph in which the results of the experiments reported in Part I. and in this paper are collected together for reference.

Table 1.

Showing Softening Temperature in °C. in Atmospheres of CO and Water-Vapour.

Material.	Atmosphere.	
	Carbon Monoxide.	Water-vapour
Cone mixture alone	1415°C.	1420°C.
A1	1420	1422
A2	1380	1345
A3	1350	1280
A4	1340	1260
A5	1320	1220

If the lowering of the temperature of softening be taken as a measure of the reducing properties of these gases, it will be seen that both carbon monoxide and water-vapour are strongly reducing in their action. Examination of the cones themselves shows that they maintain their sharp edges and display an absence of vesicular structure which, from the results reported in the previous paper[6], seems to be so characteristic of materials fired in a reducing atmos-

[6] *Vide* p. 94.

phere as compared with the same materials fired under oxidizing conditions*. While the reducing effect of carbon monoxide is very pronounced, being almost equal to that of hydrogen, the effect of water-vapour is of extraordinary interest. It will be seen from the graph that the reducing effect of water vapour is greater than that of hydrogen, which, from the technical point of view, is usually considered to be the ideal reducing gas.

In addition to the effect upon the temperature of softening, water-vapour modifies the colour of the cones in a remarkable way; the colours in this case vary from white to a very dark grey, which is almost black, and there is no appearance whatever of the red colour which seems to be so characteristic of iron-bearing materials which have been heated. On the other hand, the cones which have been heated in carbon monoxide do display this red colour.

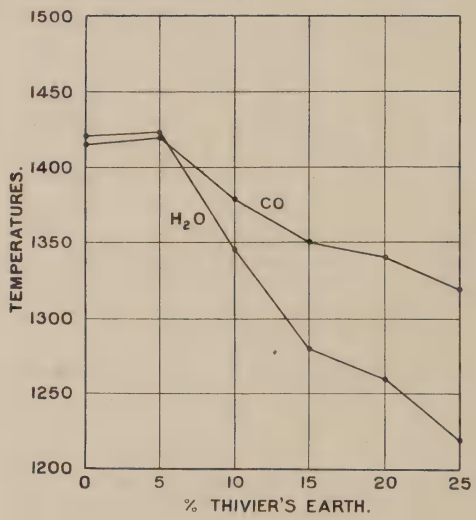


Fig. 1.

Discussion of Results.

A possible explanation of the action of carbon monoxide in these experiments may be found in the observations of G. Charpy[7] who studied the action of carbon monoxide upon iron and its oxides. He found that if iron oxide is heated in an atmosphere of carbon monoxide and in contact with a porcelain tube, a ferrous silicate is formed. This ferrous silicate is very difficult to break down. The low melting points of the ferrous silicates and their reactions

* G. H. Brown and G. A. Murray in *Tech. Paper*, 17, Bureau of Standards, (1913), state that reducing atmospheres are the cause of vesicular structure, but A V. Bleininger and E. Montgomery in *Tech. Paper* 22, Bureau of Standards (1913), find that oxidizing atmospheres give vesicular structures, thus supporting the results obtained in the present investigation.

7 G. Charpy, *Compt. Rend.*, **137**, 120-122, 1903.

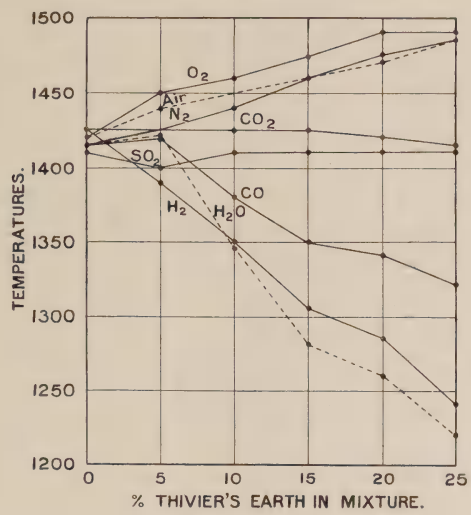


Fig. 2.

with iron to form a mass of still lower melting point, which were studied by H. H. Reiter[8], may be the explanation of the effects now obtained. In the case of water vapour*, the explanation seems to lie in the liberation of hydrogen in an active condition, which reacts with the iron of the cone material producing a low-melting silicate or mixtures of silicates.

The chemical interpretation of the results obtained by heating the experimental cones in an atmosphere of water vapour is rendered very difficult by the complexity and the number of the reactions which may be involved. R. B. Sosman[9], reviewing a number of papers upon magmatic differentiation and ore formation, states that, at the temperatures under which magmatic differentiation takes place, the properties of water are absolutely different from those displayed at ordinary temperatures; it may consist of a number of components, such as the uncombined elements hydrogen and oxygen; he instances the existence of free hydrogen and oxygen together with water-vapour in the volcanic vapours given off from the Kilauea volcano.

The action of the water vapour upon the cone mixture as reported in the present paper seems to be caused by the decomposition of the water-vapour into atomic, or ionized, hydrogen and hydroxyl (the hydroxyl radicals uniting to form hydrogen peroxide) rather than by a decomposition into hydrogen and oxygen. In

8 H. H. Reiter, *N. J. B. Min., etc.*, **22**, 185, 1906.
9 R. B. Sosman, *Economic Geology*, **19**, 584, 1924.
* Above the critical temperature, namely, 366°C., water-vapour is regarded as a gas, while steam is considered to be essentially a polyphasic system.

support of this view there is the experimental fact that the temperatures at which the cones subsided were lower in an atmosphere of water-vapour than in an atmosphere of hydrogen. This result finds an explanation in the possibility of the reduction having been performed by atomic rather than by molecular hydrogen. Further, all the conditions which favour the decomposition of water in this manner are present under the conditions of the experiment, namely, a silent discharge of electricity through the atmosphere of water vapour[10]; the action of ultra-violet light of short wave length[11] which is emitted from the sides of the furnace; the presence of refractory oxides which catalyse the reaction[12], and the emission of electrons from the furnace walls. Additional evidence in favour of this form of decomposition lies in the existence of a zone of recombination in the upper, cooler part of the furnace tube, which could always be seen when water-vapour was passing through the hot tube, and where a fairly vigorous chemical reaction seems to be taking place.

The view thus suggested may be summarised somewhat as follows :—

The water-vapour is first of all decomposed, possibly thus:

$$H_2O \rightarrow H^+ + OH^- \quad .. \quad .. \quad (1)$$

Some of the hydrogen formed acts on the iron-bearing cone mixture to produce a low melting silicate, whilst the (OH) groups combine to form H_2O_2, which, under the existing conditions, will have but a short life, decomposing thus :

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad .. \quad .. \quad (2)$$

The remaining H^+ from (1) will form molecular hydrogen and subsequently react with the oxygen of (2) to re-form more water:

$$2H_2 + O_2 = 2H_2O \quad .. \quad .. \quad (3)$$

and it is the last reaction which can actually be seen to take place above the hottest zone in the tube.

An alternative view of the first change, of course, is that the decomposition occurs according to the equation

$$2H_2O \rightarrow H_2O_2 + H_2$$

but this does not seem to provide for the additional activity of the hydrogen, to which the greater reducing effect noted with water-vapour is ascribed.

Applications.

The application of the results reported in this paper is of great interest both to the maker and to the user of refractory materials, since

10 M. Kernbaum, *Bull. Acad. Cracow*, 583, 1911.

11 M. Kernbaum, *Bull. Acad. Cracow*, 583, 1911.
A. Tian, *Transformations et équilibre chimique de l'eau et des solutions de peroxide d'hydrogene à la lumière ultra-violette, Marseille*, 1915.
W. Nernst, *Zeit. Electrochem.*, **11**, 710, 1905.
E. Warburg, *Ber. deut. phys. Ges.*, **17**, 194, 1915.

12 W. Nernst, *Zeit. anorg. Chem.*, **45**, 126, 1905.
See also J. W. Mellor, *Comp. Treatise on Inorganic and Theoretical Chemistry*, Vol. **1**, 490, 922, 1922.

carbon monoxide and water vapour are the two gases which in ordinary practice most frequently come into contact with refractory materials.

Failure of the refractory materials used in the building of the retort section of a steamed vertical retort installation may be brought about by the formation of a thin skin of iron-bearing ash upon the surface of the retort (due to coal burning there in very small quantities during the course of the operation of the plant). This iron-bearing material, existing as it does in the interstices of the surface layer of the refractory material, reacts with the excess steam in the manner indicated and so provides a flux capable of bringing about the failure of other material.

The action of water-vapour at fairly high temperatures is, undoubtedly, responsible for many of the failures which occur in the refractory linings of coke oven walls and in the retorts of a gas works plant. If either of these types of plant is heated up in the preliminary stages at too great a rate, water-vapour (from the drying brickwork), is brought into contact with heated refractory materials under conditions, which, as the experiments here reported indicate, favour the production of low melting point minerals within the material and hence the ultimate rapid failure of battery or setting. Water-vapour, which may be introduced into a kiln towards the end of firing through the agency of wet fuel or through the kiln having water logged foundations, may also have a very harmful effect upon the goods, by bringing about changes which result in a lowering of the refractoriness. It would seem from an examination of the results reported in Pt. I. and in this continuation that, in order to prevent failure of the material through the formation of low-melting iron minerals, the kiln atmosphere should be kept as oxidising as possible and as dry as possible. Similar conclusions apply to the preliminary heating up of a retort setting.

The water vapour produced from the oxidation of hydrogen compounds in the fuel itself and appearing as one of the products of combustion is always present, and must contribute largely to the ultimate and unavoidable failure of a setting.

Summary.

1. The influence of atmospheres of carbon monoxide and water-vapour respectively on the softening range of a cone mixture containing ferruginous material has been investigated.

2. Carbon monoxide has a marked reducing action and lowers the softening temperature 170°C. for a mixture containing 2·50% Fe_2O_3 and 0·085% FeO as Thivier's Earth.

3. With water-vapour, even more pronounced effects have been obtained; in fact, the action is more powerful than in an

atmosphere of hydrogen itself. The colour of the cones heated in water vapour varies from white to a very dark grey or black.

4. Tentative explanations for the reducing effects of these gases have been advanced, and the practical significance of these results to the industry has been briefly discussed.

XIII.—The Temperature Gradients obtained by Different Rates of Heating in Unfired Fireclay Bricks, between 15°C and 250°C.*

By L. S. Theobald, B.Sc., A.R.C.S., and A. T. Green.

[*Printed by permission of the Council of the British Refractories Research Association].

Introduction.

THE work contained in this paper has been undertaken by the authors as a part of their investigation of the economically safe rate of firing silica and fireclay bricks. The aim of this extended research is to reduce the time of firing needed for refractory bricks to a minimum consistent with safety and a well-burned product. That heat treatment of fireclay goods, which transforms the raw material into the finished product may be roughly divided into the three consecutive or overlapping periods: viz., (1) The Water-smoking Period; (2) The Oxidation Period; (3) The Vitrification Period. The present communication is concerned with an experimental consideration of certain phases of the first-named period.

Water-smoking, which is concerned with the changes taking place in clay goods at low temperatures, is one of the most delicate operations through which these goods pass during "burning." It has been defined as the expulsion, in a kiln, of mechanical and hygroscopic water contained in unfired products. Such an expulsion if carried out too quickly may set up strains in the material, and, in some cases, cause actual disruption. Again, the goods themselves, when placed in the kiln, may contain varying percentages of water, or, such a variation may be set up, during the initial stages of burning, by condensation of water-vapour arising from an uneveness in temperature in various parts of the kiln. Such a state of affairs may lead to decided faults creeping in during the subsequent periods of oxidation and vitrification, which may not, then, be simultaneous throughout the different parts of the kiln. This is well illustrated in Fig. 1.

This paper, by an examination of thermal gradients, occurring with different rates of heating reports definite information concerning the influence of the water in full-sized firebricks, and further, gives a basis upon which a consideration of the thermal effects occurring during the water-smoking period in fireclay bricks may be adjudged.

Previous Work.

Of the work of previous investigators, little has been found in the literature which describes any experiments made directly upon

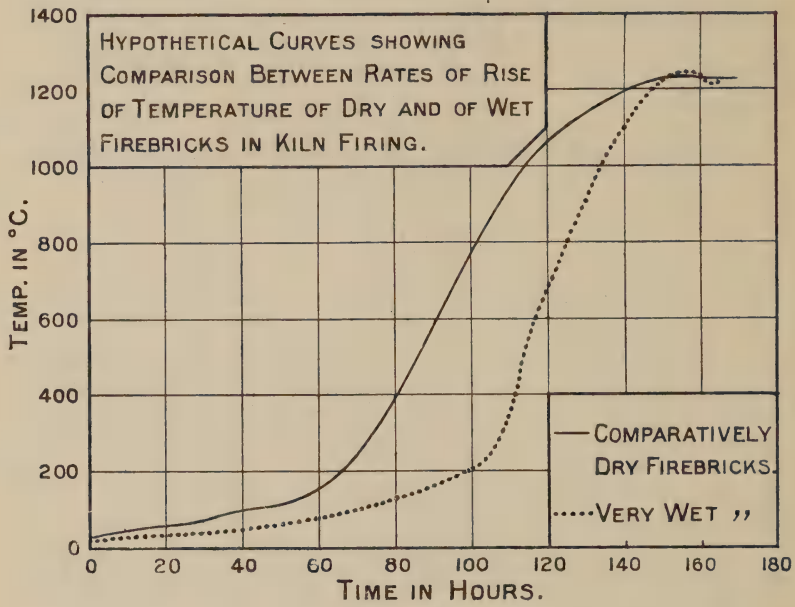


Fig. 1.

the initial period of burning refractory materials.

J. H. Kruson[1], however, in an instructive article entitled "The Standardisation of Burning" recommends a method for the determination of that draught and temperature schedule which will carry clay-ware safely through the water-smoking period in the shortest possible time.

R. F. Geller[2], in an important paper on "The Water-smoking of Clays," describes the experiments which he has carried out by a method to which the present is very similar. From the four clays studied, Geller concludes that :—

(1) In order to expedite water-smoking, it is necessary to dry the ware thoroughly and at a temperature of 100°C.

(2) Any steam produced must be promptly removed, and

(3) The rate of rise in temperature should be such that there is no great difference between the temperature of a kiln and the interior of the products which it contains.

Further, in the case of plastic clays, sufficiently dried, water-smoking should be completed in 15 hours, when heated to 300°C., provided there is an efficient circulation, a result which, in certain cases, agrees, more or less, with those about to be described.

Finally, the temperature range of water-smoking lies between 100°C. and 240°C. for a material which has been adequately dried.

Numerous other brief, but useful, notes on the water-smoking period of clays have appeared from time to time[3], but no definite experiments, other than those mentioned above, seem to have been reported.

The Materials of Experiment.

Ordinary commercial bricks, supplied in the green state, by the manufacturers of three standard products, viz., (A) Stourbridge, (B) Scottish, (C) Yorkshire, were selected for the experimental work. These materials were allowed to stand in the laboratory for several weeks, after which treatment they were considered to be adequately air-dried. Table I. shows the analyses of the bricks dried at 110°C., together with some of the properties of the air-dried bricks.

Some details concerning the manufacture of the bricks were elicited from the various firms. In the case of Brick A, the raw materials are mixed, ground, screened and then placed in the tempering tub. The grog, of which 20-25 per cent. is used, is not soaked in the water by itself. It is wetted in the tempering tub, but the conditions are so arranged that there is no danger of the grog extracting the water from the clay substance. The bricks are hand-made, after which they are allowed to dry on the drying floor twenty-four hours before setting in the kiln. No special precautions are observed in this drying, some of which takes place in the chambers of the continuous kiln. According to the manufacturer, forty-eight hours is necessary to dry the bricks "white-hard" in the Woolfe dryer.

About 20 per cent. of grog, which is wet-ground, is used in the manufacture of brick B. The clay before moulding is in a somewhat stiffer condition than is generally employed in brick manufacture. The bricks are hand-moulded and are then placed on the drying floor, being sent to the kiln whenever desired. Brick C is made to contain about 8 per cent. of grog, which is mixed dry. It is machine-made and is dried in the warm making-room for a period of about two days. As with brick A, no particular consideration is given to the drying of bricks B and C.

An examination of the texture shows that bricks A and B are very similar, being fairly open in appearance. In both bricks, besides the grog, there is a proportionately large amount of hard, rounded nodules. Brick C, as before stated, presents a much more compact structure, the grog and hard nodules possessing a far greater adhesion to the clayey matrix than is found in bricks A and B.

Apparatus and Method of Experiment.

Briefly, the method adopted in this study consists in heating

*The porosity determinations on pieces of the green bricks were successfully carried out in paraffin.

TABLE I.

	On Sample dried at 100°C.					On Sample Air-dried in Laboratory.		
Mark	SiO_2	Al_2O_3	Fe_2O_3	$Na_2O + K_2O$	Loss on Ignit.	Size of Brick in inches	Loss in Weight on heating to 120°C., 5 hours	Apparent Per cent Porosity
A	52·21	30·93	2·45	1·08	11·52	9·25 × 4·35 × 2·95	2·72%	22·6
B	49·36	36·35	1·25	1·78	9·20	9·18 × 4·62 × 3·00	1·86%	24·0
C	71·20	18·15	0·97	1·18	7·30	9·10 × 4·48 × 2·98	1·21%	21·1

an air-dried (in the laboratory), unfired brick up to a temperature of 250°C. at a definite rate and in measuring the difference in temperature which occurs between the sides and centre of the brick

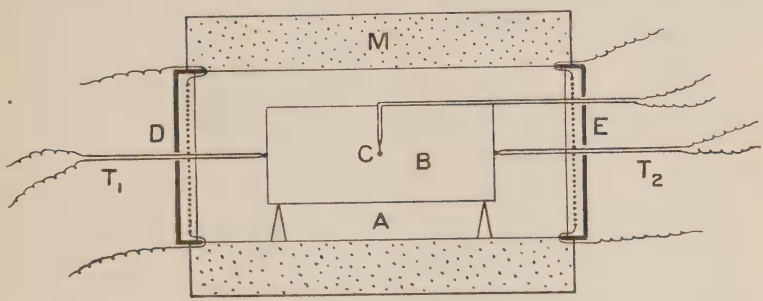


Fig. 2.

The apparatus (Fig. 2) consists of a rectangular fireclay box A, $15'' \times 7\frac{1}{2}'' \times 6\frac{1}{2}''$ internal dimensions, one end of which can be removed to allow the brick B, under investigation, to be placed in the centre. The box is wound with Nichrome wire of a suitable gauge. Twelve holes—diameter from $\frac{1}{2}''$ to $\frac{3}{4}''$—have been made in the sides and ends to allow (1) for the insertion of five base-metal thermo-couples (three only of which are shown in the sketch) and (2) for the escape of steam, and the continued entrance of fresh supplies of air. Four of the five thermo-couples, T_1, T_2, etc., are adjusted so that one touches each of the sides and ends of the brick. The free ends of the couples are connected by copper wires to a milli-voltmeter. The fifth couple, C, is fixed in the centre of the brick. In order to do this, a hole $\frac{1}{4}''$ diameter is drilled to the centre and the couple—one element of which is insulated by means of asbestos string—is placed therein. It is kept firmly in position by tightly filling the hole with some of the clay dust removed during the drilling.

The brick, carrying thermo-couple C, is placed in the centre of the box A, being raised from the bottom by means of two supports. The end of the box is cemented into position by means of a little fireclay paste. In order to ensure a uniform temperature throughout A, the ends are heated by two auxiliary heaters D and E, which are attached to covers made of fireclay. These covers are adjustable and can be made to fit just over the ends of A. This heating system is run off a source of power independent of that which supplies the wire-wound fireclay box. The usual resistances, switches, etc., control the current supply and hence the temperature of the furnace.

Loss of heat is prevented and an approximate uniformity of temperature obtained by surrounding the apparatus with a layer of diatomaceous earth, 2″ in thickness, enclosed by bricks made of

insulating material. Preliminary experiments were made to determine any irregularities of temperature on the top, bottom and sides of a brick in the box. Such irregularities were overcome, as far as possible, by thickening the walls of the box by layers of fireclay cement.

The heating of the green brick is carried out according to a definite schedule, and the rate of rise of temperature controlled by hand. With the exercise of proper care and by reading the temperatures indicated by the thermo-couples at frequent intervals, a good approximation to the scheduled temperatures can be maintained.

In each experiment the finishing temperature is 250°C., and the rates of rise of temperature are 10°C. in 15, 20, 30, 40 and in one case, 60 minutes. Readings are noted at the ends of these intervals. The foregoing rates correspond to periods of heating for $5\frac{3}{4}$, $7\frac{2}{3}$, $11\frac{1}{2}$, $15\frac{1}{2}$ and 23 hours from the temperature of the laboratory (15°C.) to the finishing temperature 250°C.

The base-metal couples were standardized against a reliable mercury-in-glass thermometer used in conjunction with a millivoltmeter. The readings on this latter scale were converted into degrees centigrade by means of the calibration curves drawn from this standardization. The mean of the temperatures, obtained from the four couples, touching the sides and ends of the brick, is adopted as the temperature of the exterior of the material under investigation. The value for the centre of the brick is obtained directly from thermocouple C.

Results.

Some twenty experiments have been completed, the results of which are most conveniently presented in the form of temperature-time curves (Figs. 3-17). Figs. 3-9 are concerned with the Stourbridge material, Figs. 10-13 with the Scottish material, and Figs. 14-16, with the Yorkshire brick. Fig. 4 deals with the behaviour of one of the Stourbridge bricks, which had been freed from its moisture by heating to 250°C. on the day previous to carrying out the experiment.

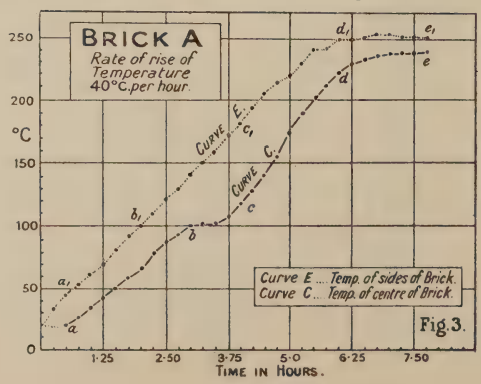


Fig. 3.

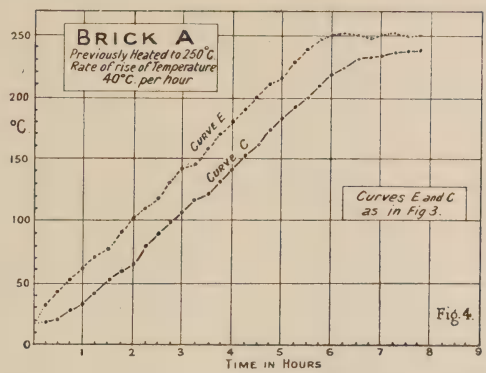


Fig. 4.

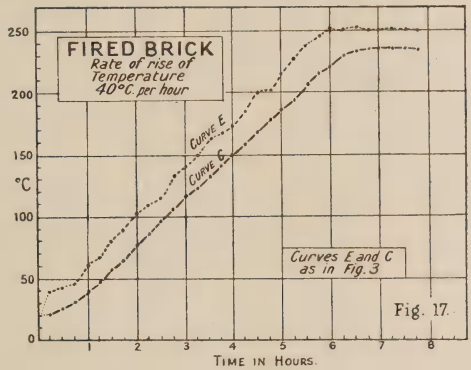


Fig. 17.

With the object of comparing the temperature diffusivities of a fired and an unfired brick, Fig. 17 was obtained. A well-fired brick made of Stourbridge fireclay—not of the same origin as the unfired material, but approximately of the same dimensions as Brick A, was used for this purpose.

Discussion of Results.

Significance of Curves. It is considered advisable to explain the significance of the temperature-time curves. For this purpose Fig. 3 can be considered. Curve E, the upper of the two curves, shows the temperatures of the exterior of the brick, at successive intervals of time. Curve C, the lower, gives the corresponding temperatures of the interior of the brick. The ordinate between the corresponding points on the two curves will give a measure of one or both of two physical phenomena, viz. :

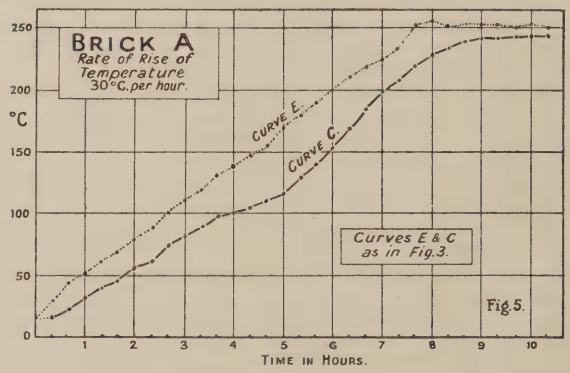
(1) The thermal conductivity, or more correctly, the temperature diffusivity[4] of the material.

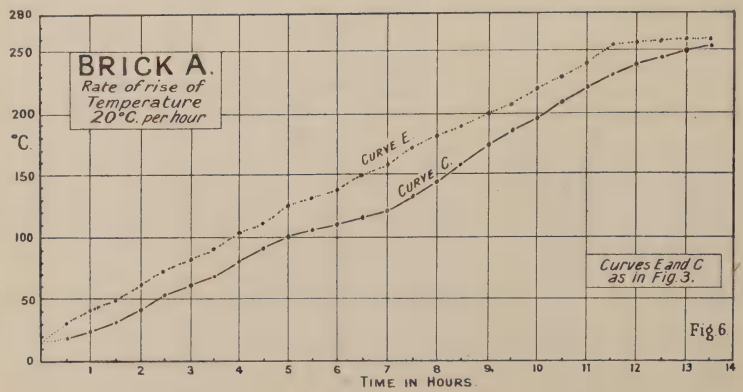
(2) The absorption of heat by the brick in the performance of

various physical and chemical changes, *i.e.*, mainly in the expulsion of water as water vapour.

Fig. 3 illustrates the effects of these two phenomena. The ordinates between the curves E and C for the range of interior temperatures *a–b*, and the corresponding range of exterior temperatures a_1–b_1 represent, in the main, the former effect.[1] The lower curve for the range *b c* shows a definite change of direction and is referred to as an "arrest." This "arrest" indicates that an additional absorption of heat is proceeding. In the case being considered, heat is being used to expel the water as vapour.

The consequence, from the point of view of the temperature-time curve is that the temperature gradient within the brick, *i.e.*, the temperature difference between the exterior and interior is greatly increased during this period of heat-absorption. In fact, the temperature "lag" induced during this period persists in a gradually decreasing measure, during the rise of exterior temperature from c_1 to d_1. It has not fully disappeared at d_1 (250°C.), although it is very small at this temperature.





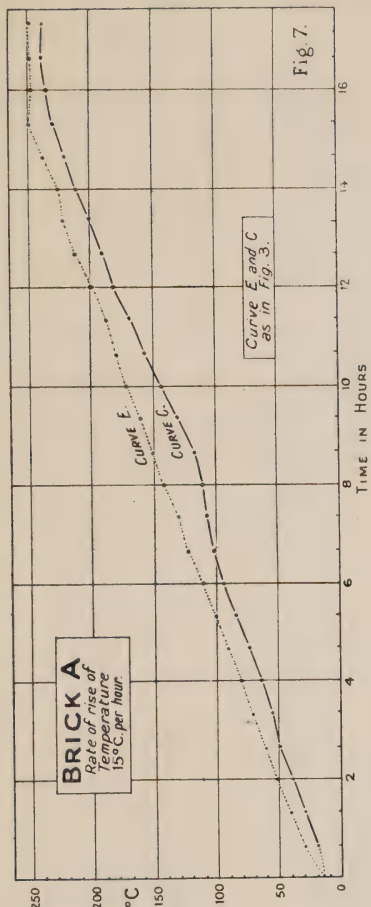


Fig. 7.

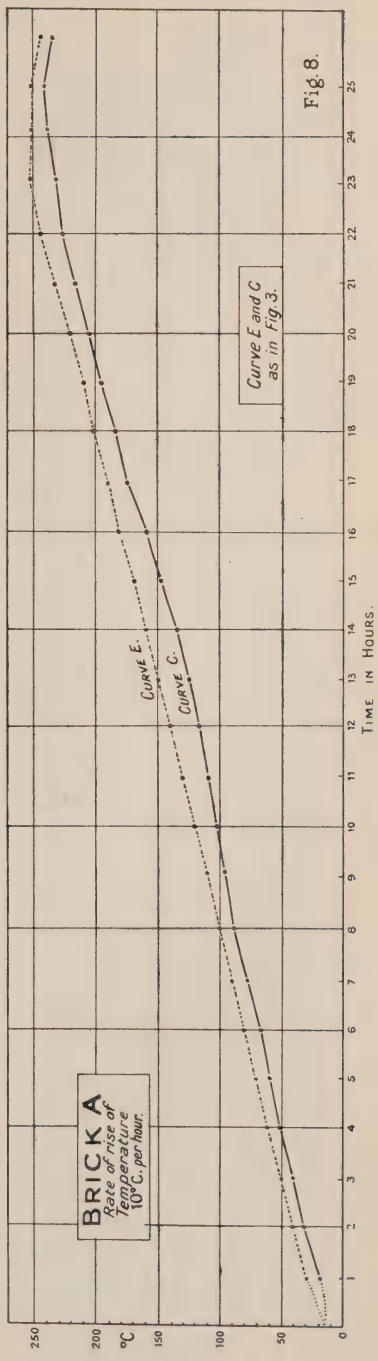


Fig. 8.

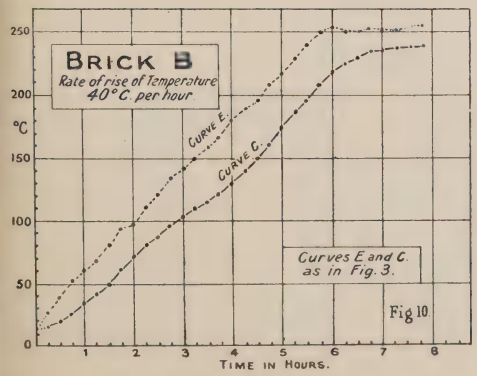
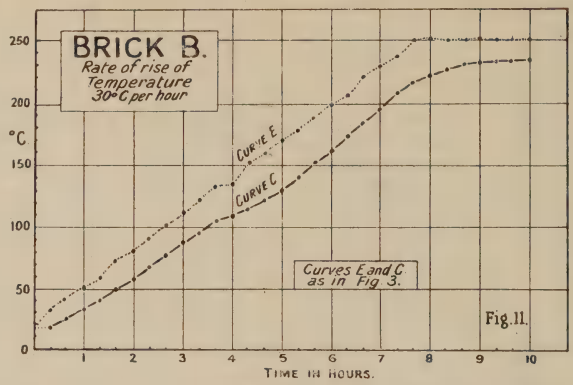
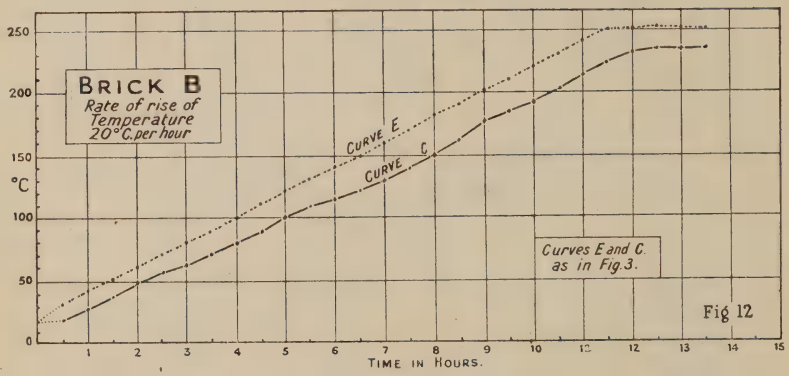


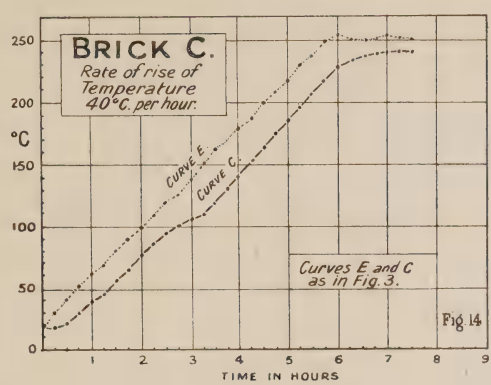
Fig. 10.

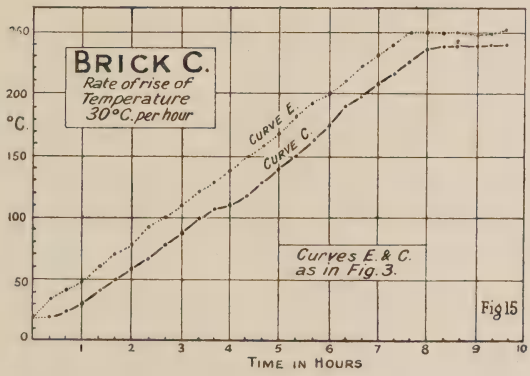


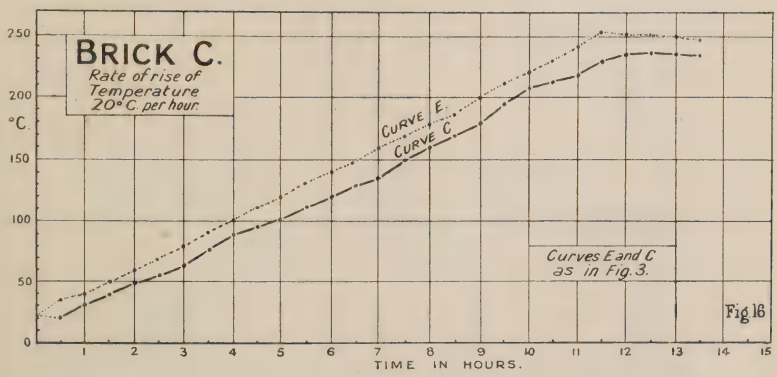


It will be observed that much useful information can be extracted from the temperature-time curves. However, further curves derived from these primary relationships appear to the authors to add considerably to this discussion. These derived curves are obtained by plotting the value of the ratio $\frac{\theta_1-\theta_2}{\theta_1}$ called the "gradient-ratio"—against θ_1, where θ_1 is the temperature of the exterior of the brick at a specific time, and θ_2 the temperature of the interior at the same time. Since the time factor is included in the gradient-ratio, these curves are merely another form of the temperature-time relationships. One of the greatest advantages of the derived curves is that the temperature-time relationships for all the different rates of heating can be conveniently plotted on one figure, which fact allows an immediate comparison of the effects of the various rates of heating to be made. The "gradient-ratio" curves are drawn in Figs. 18—21.

It is well-known that considerable strains may be set up in clay products during the water-smoking period. These strains may be due to a variety of causes which include (1) a rapid change







of water into water-vapour, with the consequent great increase in the volume of the fluid, the pores of the material being inadequate to take away the water-vapour, at a rate quick enough to prevent strain ; (2) the volume change, due to the re-arrangement of clay

particles during the elimination of water, and to the true thermal expansion of these constituent clay particles and grog. The extent of this strain will depend upon many factors—chiefly "material factors"—the more important of which are (*a*) the nature of the fireclay, (*b*) the nature of the adhesion of grog and clayey matrix, and (*c*) the nature and amount of pore-spaces. A quantitative definition of the extent of thermal strain would require the accumulation of considerable experimental data, at present not investigated. For these reasons, the arguments and comparisons, which are based on the θ–t and gradient-ratio curves are somewhat limited. However the temperature difference between the exterior and interior of the brick, or better, the gradient-ratio, is the most important term in that function, which circumscribes the magnitude of thermal strain. A study of the curves, therefore, will throw some light on the safe rate of heating fireclay bricks from ordinary temperatures to 250°C.

Information Derived from the curves.

A comparison of Figs. 3, 5, 6, 7 and 8, together with a consideration of the gradient-ratio curves of Fig. 18, defines the quantitative effect of a decrease in the rate of heating on the temperature gradient between the exterior and interior of Brick A. A full description of this comparison is unnecessary; Table II will illustrate the point in question. In this table the maximum temperature differences are reported for different rates of heating. These maximum values are obtained after a consideration of the gradient-ratio, the exterior temperature giving the maximum gradient-ratio being taken as the basis.

A preliminary indication of the quantitative effect of water in causing this maximum temperature difference can be readily obtained either by comparison of Figs. 3 and 4 or curves 1 and 2 of Fig. 18. The brick used in the determination of Fig. 4 because of its treatment contained only a negligible quantity of mechanical and hygroscopic water, and, of a consequence, the temperature

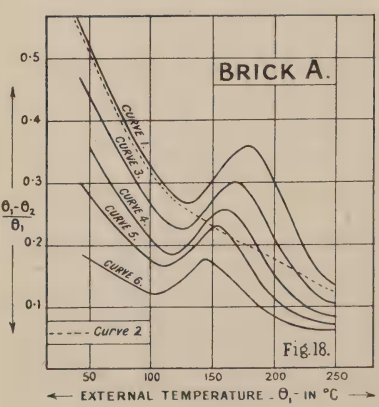


Fig. 18.

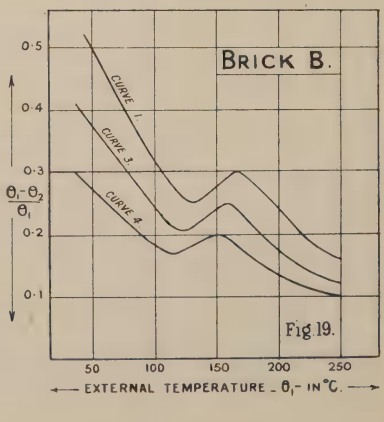


Fig. 19.

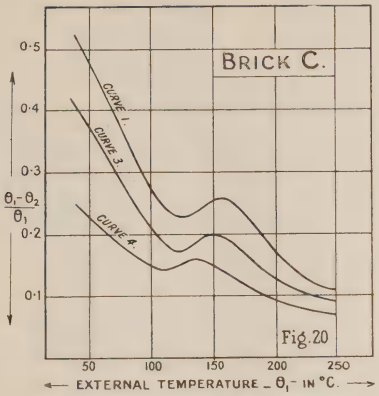


Fig. 20

difference occurring with an exterior temperature of 184°C. is 37°C. for a rate of heating of 40°C. per hour. This contrasts strongly with the maximum temperature difference of 66°C. obtained when 2·72 per cent. of water is present. The simple hyperbolic nature of Curve 2 in Fig. 18, allows hypothetical curves showing the behaviour of the brick containing no water for different rates of heating to be drawn. From these it is easy to calculate approximate, comparable temperature differences for given exterior temperatures, for different rates of heating. Such values together with approximate gradient-ratios for these values are reported in Table II. and afford a very interesting comparison.

The foregoing remarks are specifically concerned with the effect of water in brick A. It is advantageous to consider the three bricks from the point of view of their water content. The θ–t curves of brick B and C show a much less defined "arrest" than do the curves for brick A. The existence of some relationship between the water content, rate of heating and gradient-ratio is indicated by a consideration of the curves of Figs. 18, 19, and 20, and Table II. In illustration, it is noted in this table that the difference between the maximum temperature gradient (Y) and the calculated approximate temperature difference when water is absent (Z). There is a definite proportionality between this difference (for a specific rate of heating) and the water content, when comparing bricks A, B and C. In fact, this comparison suggests that there is a simple linear relationship between the difference, (Y–Z), and the water content of unfired fireclay bricks.

The experiments, in most cases, have not been stopped when 250°C. has been reached, but have been carried on by maintaining this exterior temperature constant for two hours. By such a procedure, the interior temperature gradually approaches an almost constant value. Because of the many difficulties encountered in maintaining the exterior temperature constant, the accurate

TABLE II.

Mark	Water Present					Water Absent		
	Rate of Heating °C. per hour	Ext. Temp. for Max. Temp. Diff.	Maximum Temp. Diff. Y °C.	Gradient Ratio	Water Content per cent	Calc. Temp. Diff. Water Absent Z °C.	Gradient Ratio	(Y–Z)°C.
A	40	184	66	0·36	2·72	37	0·20	29
	30	173	53	0·31		30	0·17	23
	20	162	41	0·25		21	0·13	20
	15	153	35	0·23		17	0·11	18
	10	143	24	0·17		12	0·08	12
B	40	167	50	0·30	1·86	33	0·20	17
	30	158	40	0·25		24	0·15	16
	20	150	32	0·20		20	0·13	12
C	40	158	41	0·26	1·21	28	0·18	13
	30	151	32	0·21		20	0·13	12
	20	140	23	0·16		15	0·10	8

definition of the interior was rendered very difficult. An estimate, however, gives for brick A, 13°–15°C. as the difference between the exterior and interior, for brick B, 16·5°C., for brick C, 13–14·5°C., and for the fired brick, 14·5°C. These approximate results are obtained with rates of heating between 40° and 20°C. per hour.

Such temperature differences correspond to gradient-ratios of 0·06 for brick A, 0·066 for brick B, 0·056 for brick C, and 0·056 for the fired brick. For approximate thermal equilibrium to be maintained within the bricks throughout the rise of temperature from 20°–250°C., these pseudo-equilibrium values of the gradient-ratio should practically obtain during this period. From a consideration of Figs. 18, 19, 20, it would appear that brick A requires, at least, 50 hours to approximate to this pseudo-equilibrium, brick B, at least 35 hours, and brick C, roughly 28 hours. These times correspond to rates of rise of temperature of about 4·5°C. per hour for brick A, 6·6°C. per hour for brick B, and 8·1°C. per hour for brick C.

These "pseudo-equilibrium" rates of rise of temperature appear to be too low to be justified. Thus, at an exterior temperature of 140°C., the equilibrium value of the interior temperature would be 132°C. The experience resulting from contact with this work suggests, however, that the interior temperature could be as low as, say, 120°C. without any undue strains being set up in the material. In other words, 28 hours for brick A, 17 hours for B, and 13·5 hours for C, in the circumstances of the experiment, would serve adequately to allow the brick to reach 250°C. without causing undue strain in the material. In the actual firing of Bricks A and B in continuous kilns (of different designs, of course), 24 hours and 12½ hours respectively were taken to reach 250°C. These data although in good agreement with those derived from experiment, are limited in value, since they are based on temperature readings taken from one position only in the kiln.

A consideration of the "gradient-ratio" curves shows that when the maximum value of the ratio is obtained, the interior temperature of the brick lies between 117° and 121°C. This fact suggests that all the mechanical and hygroscopic water has been

TABLE III.

Rate of heating in °C. per hour	Time taken to raise brick from 100°C. (exterior) to 120°C. (interior) in hours.		
	Brick A.	Brick B.	Brick C.
40 ..	2·10	1·68	1·45
30 ..	2·43	1·93	1·70
20 ..	3·10	2·50	2·00
15 ..	3·52	—	—
10 ..	4·30	—	—

expelled when this interior temperature has been reached. Also, it may be reasonably assumed that practically the whole of the water leaves the brick between the temperatures of 100°C. on the exterior and 120°C. in the interior of the brick. The time required to establish these conditions varies with (*a*) the temperature diffusivity of the material; (*b*) the amount of water present and (*c*) the rate of heating of the brick. Data concerning the time taken are contained in Table III.

From the data of Table III., the rate of escape of steam per minute can be obtained. This information is reported in Table

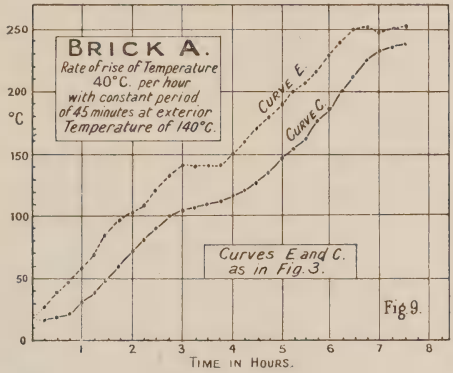
TABLE IV.

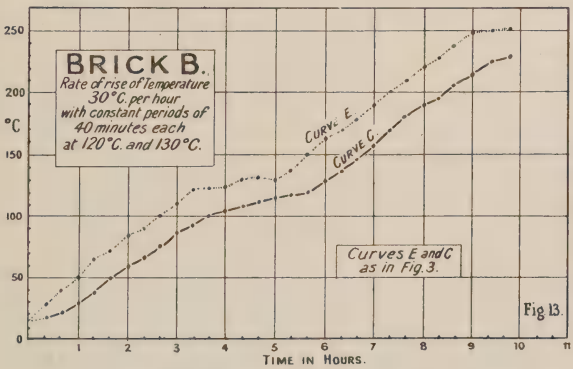
Mark	Approx. Weight of Water per brick in grams.	Approx. Volume of Steam formed per brick in ccs.	Rate of Escape of Steam in ccs. per min.				
			40°C/hr.	30°C/hr.	20°C/hr.	15°C/hr.	10°C/hr.
A	90	150,000	1210	1040	860	710	580
B	65	108,500	1085	980	720	—	—
C	40	66,800	770	650	550	—	—

IV. A consideration of this factor in the water-smoking of clay is both interesting and useful since it shows what a considerable volume of steam can be formed within the brick and the time taken for its escape. It is, for instance, rather startling to think that 150,000 ccs.—nearly one hundred times the volume of the brick—of steam are formed within each Brick A. The formation and escape of such a volume in too short a time, must, itself cause considerable strain. In our experiments no attempt has been made to control the draught, and consequently, the escape of steam, but we assume that the steam is carried from the apparatus quickly and that it does not condense, to any extent, on the brick. This is by no means the case in firing practice and, consequently, a set of factors is introduced which may cause serious faults and losses in the burning. Where the conditions for condensation do exist, the length of time necessary for water-smoking is very much increased. For the complete removal of the water-vapour in practice, a draught is generally necessary. Consequently, the behaviour of this draught may affect considerably the time factor of the operation. The relation between temperature gradient, rate of heating and conditions governing draught supply will form the subject of a future investigation of which the present scheme of work and the results herein reported form a basis.

It would appear that the maintenance of an adequate constant temperature during the period of evolution of steam would be an

effective method of preventing the production of large strains. θ–t curves based on this have been obtained for brick A (Fig. 9) and brick B. (Fig. 13). These curves, which are self-explanatory show a decided decrease in gradient ratio because of this treatment. Thus, brick A at the end of 45 minutes at an exterior temperature of 140°C. has a gradient-ratio of 0·19 instead of 0·28 which is obtained by the ordinary rate of rise of temperature of 40°C. per hour. In the case of brick B, the exterior temperature of which had been maintained constant at 120°C. for 40 minutes and 130°C. for 40 minutes the gradient ratio at the end of the latter period is 0·12, while in the normal rate of rise of temperature of 30°C. per hour, the gradient-ratio at 130°C. is 0·23.



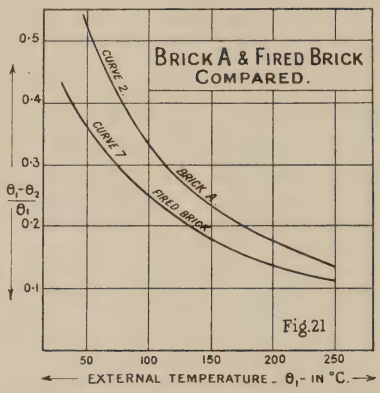


The Comparative Temperature Diffusivities of the Materials.

Fig. 21 contains gradient-ratio curves of brick A and the fired brick. These materials possess approximately equal dimensions and, consequently, the two curves can be directly compared. The conception of temperature diffusivity[4] contains the three

terms, time, temperature and distance and since time and distance are, in the case in question, constant, the temperature, or gradient-ratios of curves 2 and 7 are directly comparable at any particular temperature. Thus, we see that the fired brick has a considerably higher diffusivity than brick A, since the gradient-ratios of Curve 7 are considerably lower than those of Curve 2.

From a study of the probability integral we note that within the limits of our experiments $K=C/G^2$ approximately, where K



is the temperature diffusivity and G is the gradient-ratio, C being a constant. From the curves of Fig. 21, then, it appears that the fired brick has diffusivity about 80% greater than that of the unfired brick A at 100°C. and 50% greater at 250°C. These curves also indicate that the rate of increase of diffusivity with temperature is greater in the case of the unfired material than in the case of the fired goods. Approximate comparisons show that unfired bricks A and B have practically the same diffusivities, while brick C has a higher diffusivity than either of the former bricks. This is interesting since brick C is the only one which has been machine made.

Summary.

(1) The temperature-gradients obtained by different rates of heating in unfired fireclay bricks between 15° and 250°C. have been investigated by a method which determines the exterior and interior temperatures of the unfired brick submitted to various rates of heating in a specially designed apparatus.

(2) From a consideration of the temperature-time curves, both experimental and derived, the important effect of mechanically-held moisture in the unfired brick and its expulsion have been examined.

(3) From data obtained, the minimum time required for the safe rate of heating the green bricks to a temperature of 250°C. has been considered for the three types of bricks investigated under the particular conditions described.

(4) The temperature diffusivities of the materials used are also briefly considered.

The authors take this opportunity of thanking Mr. H. Edwards of the Testing Department of the Central School of Science and Technology, Stoke-on-Trent, for much help in various parts of the experimental work.

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XIV.—An Investigation of the Changes taking place duirng the Industrial Burning of Fireclay Bricks.*

A. T. Green and L. S. Theobald, B.Sc., A.R.C S.

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Introduction.

Soon after the research on the firing of fireclay goods was commenced, it was suggested to the authors by Dr. Mellor, that much valuable information would be obtained by a study of the bricks actually drawn from a kiln, at various times, during the process of burning. Accordingly, arrangements were made with certain manufacturers of representative products to achieve this end. By reason of their courtesy and help the arrangements were fulfilled with considerable success, and a detailed examination of the progress of the various firings rendered possible.

Two burns, with each of two different types of fireclay brick,—one from Stourbridge, and the other from Scotland—have been studied. These four series of samples form a kind of standard, which will be of great help in the actual firings on the large scale,—the main portion of the research. Also, it is believed that, hitherto, no data derived from the actual trials withdrawn at intervals during a complete burn have been published, a circumstance which adds greater interest to this work.

Description of the Arrangements.

The usual grades of firebrick products were taken as the subject of the experiment. The analyses, making and drying, etc. of the Stourbridge and Scottish material are included in a previous paper by the present authors[1]. Bricks were drawn from the kiln during a normal burn. no special circumstances being attached to this procedure except a convenient arrangement of setting the experimental material. The only position available for this, extended from the centre of the wicket towards the middle of the chamber or kiln. The actual setting, withdrawal and temperature readings were kindly made by the manufacturers, who, at no little inconvenience did their best to conform to the conditions requested of them.

Two complete series, *i.e.*, Series A and Series P, were obtained from the Stourbridge manufacturer. Series A was burned in a coal-fired continuous kiln. A double row of bricks, placed on end, stetching from the wicket to the interior of the chamber, formed the test batch. The design of the kiln was such that the direction of the draught, and therefore, of the flame, took a course away from the special setting. These experimental bricks, there-

fore, obtained a "clean fire." Temperature measurements were obtained by means of a rare metal thermocouple, placed in a fixed position well inside the special setting. The readings were taken on a continuous recorder. This temperature record is shown in Fig. 1. The samples were drawn at intervals of eight hours from the start to the finish of the run and one was withdrawn during the cooling period at about 1,000°C., after which further with-

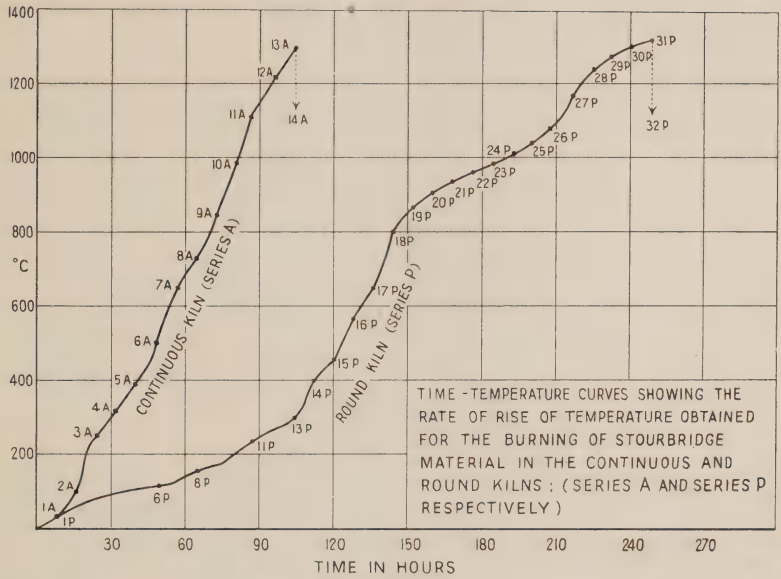


Fig. 1.

drawals were considered to serve no useful purpose.

The bricks of Series P were made from the same material and under the same conditions as those of Series A. They were, however, fired in a round kiln. A line of bricks, each on its end, was set in two rows from a position near the periphery to the centre of the kiln. The thermocouple in this case was set in one position during the whole run, *i.e.*, up against the face of the first sample. Fig. 1 shows the temperature-time chart for this run. The pull from the stack was perpendicular to the setting. This does not, however, define the actual course of the draught inside the kiln itself. As in the previous run, the samples were taken every eight hours, and one was obtained during the cooling period. In the case of the continuous kiln, 14 samples were obtained; from the round kiln, 32 samples resulted. However, because of the long duration of the water-smoking period in the round kiln, many of the samples belong to this period—see Table 9.

In the case of the Scottish bricks (Series A.G. and Series G), a gas-fired continuous kiln was the type in use

at the particular works in question. Two rows of bricks were placed at the centre of the wicket and extended into the interior of the kiln. The setting occurred in the centre of the chamber and at a height of 3 ft. from the floor. This arrangement gave conditions differing somewhat from those which obtained in the case of the Stourbridge bricks (continuous kiln), the hot gases and in a later portion of the run, the flames actually coming into contact with the bricks. The top row of bricks was the first to be drawn and the withdrawal took place every 5 hours, after, what has been described by the manufacturers, as the "benefit period." During this period of some 8 to 15 hours, the setting receives a certain amount of heat by the passage of hot gases from adjoining chambers, which were already under fire. It should also be noticed that in the method of firing adopted in this case, the gas is not introduced into a particular chamber until the bricks therein have already reached a temperature of 800° (bright redness). Series A.G. and Series G were completed in the same kiln at different firings. The temperatures were measured by means of a thermocouple up to 1,000°, and by an optical pyrometer of the wedge type above this temperature. The temperature-time curves for Series G and Series A.G. are shown in Figs. 2A and 2.

In all cases too great a reliance cannot be placed on the actual figures given for the temperatures. Reasoning based on the actual

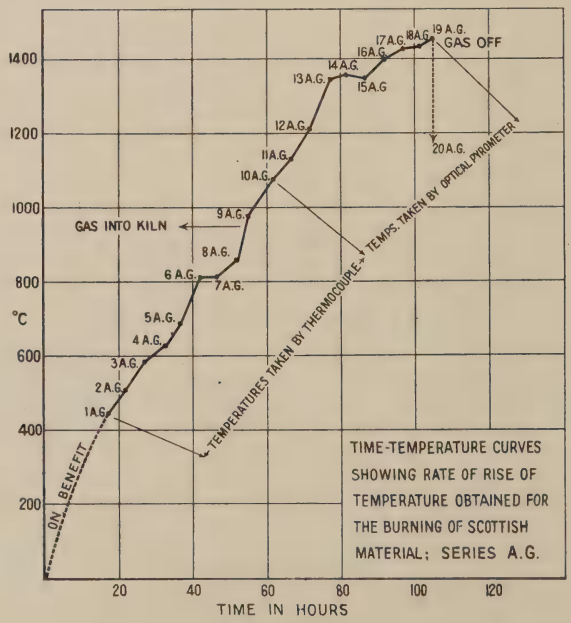


Fig. 2.

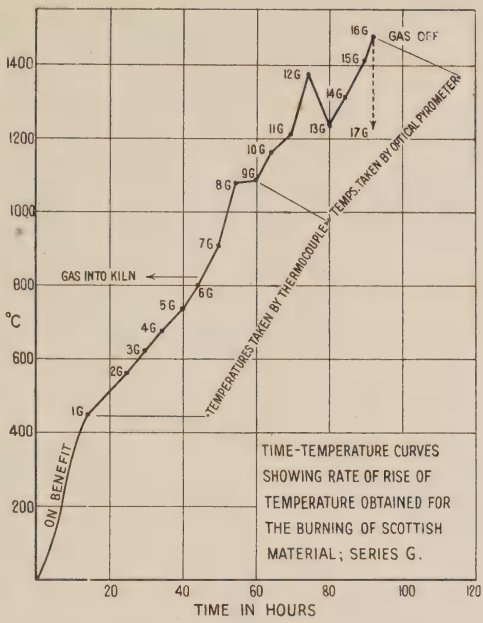


Fig. 2A.

data obtained from the samples shows that in some instances they are very inaccurate. Again, the thermocouple reading may not correspond to the temperature of the bricks, owing to local variations. These facts must be borne in mind throughout this work, both in the consideration of the curves and the discussion which follows them. Indeed, considering the uncertainty it is perhaps surprising that the various points of interest have been indicated so well.

Examination of the Specimens.

The various bricks of the different series were first measured and their surfaces described. They were then broken across at the centre and perpendicular to the length. The interiors were examined, in the first place with regard to the oxidation of the carbonaceous matters, and secondly, with regard to the other changes which became apparent. Colour photographs of the surfaces and of the interiors of half-bricks were kindly taken by our colleague Mr. A. E. J. Vickers, B.Sc. The remaining half-bricks were used for the determination of the reported data of specific gravity, porosity and "loss on ignition."

Specific Gravity.

A definite portion of the half-brick, corresponding as nearly as possible to the centre of the brick itself, was removed and ground

by hand in a stoneware mortar to the degree of fineness requisite for the determination of true specific gravity. Portions of the surface —to a depth not greater than 0·5 cm.—were also removed from the various parts of the brick and ground as before. Fairly representative samples of the interior and exterior portions of each brick were thus obtained and the specific gravity of each was separately determined using paraffin as the liquid. Each sample was dried at 110° for three hours to remove any moisture, accumulated by exposure to the air of the laboratory and then 10-15 grms. taken for each of the determinations, which were carried out in duplicate. The usual bottle method was employed and the determinations were carried out at a definite temperature—20° or 25°—according to the time of the year. Air bubbles were removed by means of a water pump which reduced the pressure down to 7-in.–8-in. of water. All the measurements were referred to the density of water at 4°C. taken as unity.

Paraffin appears to be an excellent medium for ordinary determinations of specific gravity, both of the raw and the fired clay, although, of course, the specific gravity of each fresh sample of this liquid must be found. The alteration in density of the paraffin contained in a desiccator submitted, for 4 hours to the reduced pressure used for the removal of air was so small as to be negligible in these determinations.

The maximum variation between two determinations on the same sample was 0·4%: generally, however, the variation was much less than this, viz., 0·1-0·2%. The values obtained which are reported in Tables 1, 2 and 3 have been plotted against the temperature of withdrawal and are shown in Figs. 3, 4 and 5.

The measurement of the variation in the porosity of clay products of differing heat treatments indicates some of the changes taking

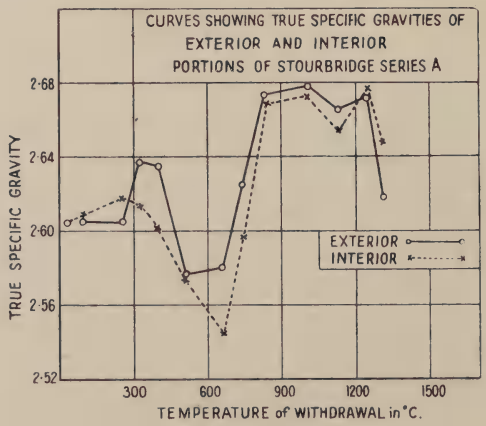


Fig. 3.

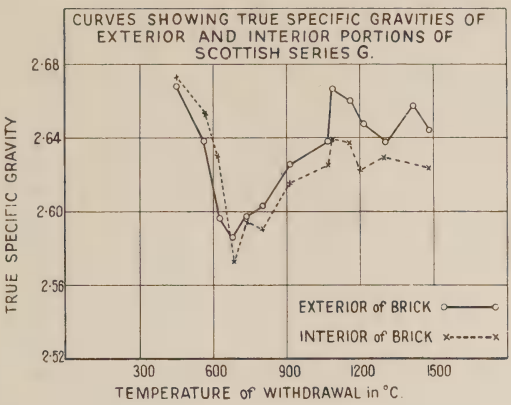


Fig. 4.

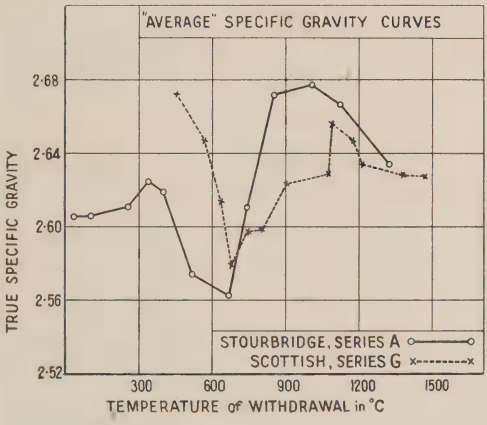


Fig. 5.

place in the physical structure of the material[2], during firing but, because of their complexity, it cannot define the nature of these changes. However, Bleininger and Moore[3], following the suggestions of previous investigators[4] have asserted the value of true specific gravity measurements in the elucidation of these changes. The variation in specific gravity is, according to these workers, the cumulative effect, in the main, of four causes, viz., (1) chemical reactions; (2) polymorphic changes; (3) fusion; (4) crystallization. In the light of present knowledge it is possible to give definition to some of the variations in the specific gravity data obtained, although many speculations are necessary in certain fields. Particularly is this so in the vitrification range.

Consider the general features of Figs. 3 and 4 which show the variation in the true specific gravity of the interior and exterior portions of the samples of the Stourbridge Series A and the Scottish Series G. Up to 300°C. with Series A, the true specific gravity of the interior portions appears to be slightly higher than that of the exterior mass. This is difficult to explain. At 320°C. there is a definite increase in the value for the exterior, which corresponds to the first detection of a change in the superficial colour. At this temperature, then, it may be that there is a breakdown of the carbonaceous matter, and some of the more volatile constituents are driven off, with the noted increase in specific gravity. It must be mentioned that this temperature, *i.e.*, 320°C., does not agree with that one obtained in an experimental investigation in a small muffle. A first change of colour in this case is noted in the vicinity of 500°C. (see remark on temperatures, p 126). The curves now reach a minimum in the neighbourhood of 600°C. (probably about 580°C. for the exterior portion of Series A, 640°C. for the interior Series A; for Series G, 670°C.). This is definitely associated with the change in the constitution of the kaolinite molecule[5], with the consequent evolution of the water of constitution. In this connection, it is interesting to note that the decrease in specific gravity from the maximum at about 400°C. to the minimum in the neighbourhood of 600°C. is 0·09 for Series A and 0·10 for Series G. The ratio of these two decrements is practically proportional to the ratio of the calculated quantities of clay substance in the two products. The curves, now rise to a maximum in the neighbourhood of 1,000°C. (*i.e.*, 990°C. for Series A, 1,085°C. for Series G). A definite change in the constitution of one or more of the constituents of the aggregate is recognised at this temperature. According to Mellor and others[6], this corresponds to the polymerization of the alumina molecule.

During the period from 600°C. to 1,000°C., oxidation has been progressing and, consequently, such chemical reactions have had definite effects on the values of the true specific gravity.

The vitrification range commences at a temperature in the neighbourhood of 950°. This range is very important to the manufacturer, from the points of view of (1) the character of the finished product; (2) the extent of the duration of this period, with the consequent economy or otherwise in fuel consumption. Bleininger[3] defines the vitrification of clays as the progressive partial fusion of the various mineral constituents, governed by the mineral composition of the body as a whole, the size of the grain, and the structure of the ware for which the clay is employed.

Again, according to the last-named investigator, complete vitrification results when all the pores are filled up. It has been abundantly proved that most silicates increase in volume on fusion, and, consequently, the density is decreased, so that during the process of vitrification of clay products a decrease in

density is to be anticipated, a fact which was realized by early workers including Laurent[7], Brogniart[8] and Rose[9]. Further, the rate of decrease in specific gravity forms some criterion of the progress of vitrification. In fact, Bleininger and Moore[3] state that the more rapid the fall in specific gravity the more rapid will be the rate of vitrification and the shorter will be the vitrification range. Applying these principles to the data of this paper, it is readily noted in the case of the Stourbridge product that between 990° and 1,220°C. the rate of decrease of density is not particularly pronounced and, consequently, although vitrification is proceeding, the rate is comparatively slow. From 1,220° to 1,300°, however, this rate is greatly increased, in fact, it may be reasonably assumed that this period is the one of the maximum speed of vitrification from the standpoint of the finished product. In the case of the Scottish material, the range of maximum vitrification is well indicated as being between 1,085°-1,310°C. After this period, there appears to be an increase in specific gravity, the interpretation of which is obscure, although it may correspond to the formation of sillimanite, or, according to Bowen and Greig, mullite. The vitrification phenomena may, therefore, be somewhat masked by such a chemical phenomenon. Although it is considered advisable to defer the consideration of the time factor until a later portion of the discussion, it may be well to point out here that the time taken with the Stourbridge material to progress from 990° to 1,220°C. is 16 hours, from 1,220°-1,300°, 8 hours, whereas with the Scottish material 25 hours was expended in raising the goods from 1,085°-1,310°C. another 7·5 hours being taken to reach the final temperature of 1,480°C. However, in the case of the Scottish material, the heat treatment is much more severe, since between the times of effecting the temperatures of 1,085° and 1,310° the kiln has once reached a temperature of 1,375°C. Further, it would seem that the Scottish material is capable of much greater vitrification before the temperature of 1,220°C. is reached. This fact is somewhat vindicated by the analysis of the two firebricks in the green state, which shows the Scottish material to include about 11% of felspathic substance and the Stourbridge product 6% of such substance in the green state.

As already stated, a sample brick was taken from the kiln, after the "fire," during the cooling period at a temperature within the vicinity of 1,000°C. Tables 1, 2 and 3 include the specific gravity determinations on such samples. In all cases, there appears to be a definite increase in the density of this material as compared with the last sample drawn during the actual firing. Thus with Stourbridge Series A this increase is from 2·631 to 2·647 (taking the average of the interior and exterior data); for Stourbridge Series P the increase is from 2·661-2·669; for Scottish Series G from 2·633 to 2·658. This increase in density may be due to crystallization of mineral constituents from the viscous

material during the cooling down. In any case, it defines the fact that a definite change takes place during the cooling, and that the rate of cooling down to a temperature of, at least, 1,000°C. must have a very important effect on the constitution, and, therefore, the ultimate properties of the product. Bricks which have been cooled down very quickly from the vitrification range possess a very brittle structure, and the conclusion can, therefore, be drawn that the actions which take place during the cooling down to 1,000°C., define, in no small measure, the ultimate mechanical strength of the brick.

During the major portion of the burn there appears to be very appreciable differences between the densities of the interior and exterior portions of the bricks. From the nature of the actions on the surface of the brick and in the interior it cannot be thought that the eventual products will be constitutionally homogeneous. It is surprising therefore to note that, for all practical purposes, two out of the three samples obtained during the cooling period have the same density of the interior as of the exterior. In the third instance, it is seen that the difference between the exterior and interior portions has been considerably reduced. This appears to emphasize the importance of the "cooling" period.

POROSITY.

The term "percentage porosity" in reference to a refractory material indicates a measure of the volume of the voids and interstices interspersed throughout the material. It gives little information regarding the size, contour and disposition of the pores. Again, percentage porosity may refer to (*a*) the total volume of the pores, to which a liquid—in these experiments, paraffin—can gain access, under the conditions of experiment or (*b*) the total volume of the pores, to some of which—called sealed pores—the paraffin cannot gain access. The first type is referred to as (*a*) the apparent percentage porosity and the second type (*b*) the true percentage porosity. The technique of porosity determinations has been the subject of a series of admirable researches by Washburn[11] and his co-workers, and their work has been particularly useful in formulating a conception of the approximate error in the present work. In the present work, the usual method[12] of measuring the apparent porosity was used. Pieces, weighing approximately 80 grams were selected from the interior and the exterior—preferably a corner in the latter case—of the sample. The apparent porosity was calculated from the data (1) the weight of the dry sample, (2) the weight of the sample thoroughly soaked in paraffin, (3) the weight of the sample suspended in paraffin. The soaking operation was carried out by fmmersion in paraffin at approximately 40°C. for five or six hours, iollowed by a stringent elimination of air bubbles by evacuation and standing under reduced pressure over-night. The approximate

error in such a determination appears to be about 2% of the value obtained; or in other words, the value itself is approximately correct to $\pm 0{\cdot}4$. The true percentage porosity is determined from the data of the true specific gravity and the apparent specific gravity; this latter being obtained by means of a computation based on the same data as the apparent percentage porosity.

Porosity determinations have been the mainspring of a considerable number of investigations concerning the effect of heat treatment on the nature of clay products. Particularly is this so in reference to the vitrification of clays. In many of the researches the rate of change of apparent porosity is taken as an indication

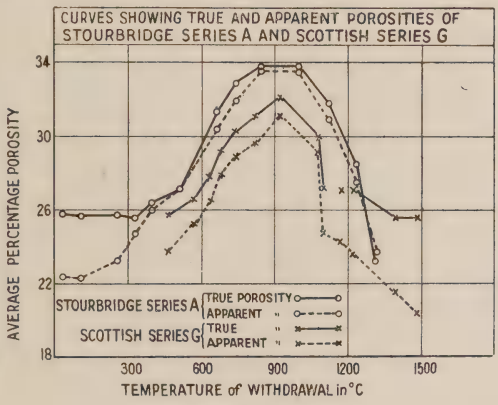
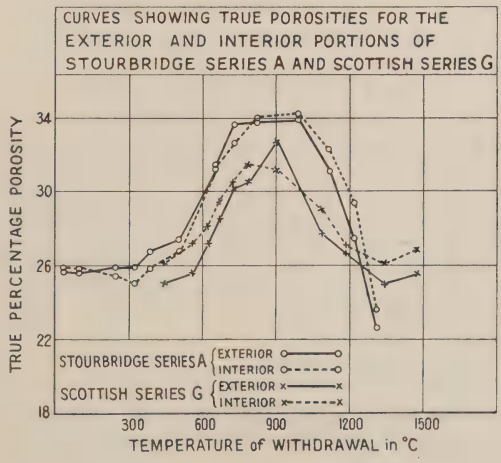


Fig. 6.



of the rate of vitrification[2]. This is a good indication, but to the present authors, it seems that the rate of change of apparent porosity together with the rate of formation of sealed pores effects a better criterion of the rate and extent of vitrification.

Consider Fig. 6, in which the true and apparent porosities (*i.e.*, the average of the interior and exterior data) of the Stourbridge Series A and the Scottish Series G are plotted against temperatures of withdrawal. With the Stourbridge material there is an appreciable difference between the true and apparent porosities up to 320°. This seems to be due to the fact that water persists in the material up to this temperature, filling up some of the pores to which the paraffin does not gain access. Such a state of affairs is also accentuated by the non-miscibility of paraffin and water. This is well in keeping with the conditions of the kiln atmosphere up to this temperature. The porosity rises at a very rapid rate up to a maximum of about 900°C. This is due to the chemical reactions chiefly associated with the burning out of carbonaceous matter and the change in the constitution of the kaolinite, with the consequent effect on the physical structure of the products. In this connection, experiments conducted by the present authors show that for practical purposes maximum porosity can be obtained by continued heating at 600° in the atmosphere of an ordinary laboratory muffle furnace. This maximum porosity is practically maintained up to a temperature in the neighbourhood of 800°C.

The decrease in porosity from 900° to the finishing temperature is, in the main, associated with vitrification. In the case of both materials, the rate of decrease of apparent porosity is very pronounced from temperatures in the vicinity of 1,050°C. In the argument based on specific gravity data it was stated that the Scottish material appeared to have a greater rate of vitrification at the temperatures below 1,200°C. This is also indicated in the porosity curves under discussion. It can be further argued that the amount of vitrification in the Scottish material is much greater since during the last period of the fire a considerable volume of sealed pores is formed, whereas up to the finishing temperature in the case of the Stourbridge product the volume of sealed pores is negligible. These sealed pores are formed by small quantities of gas evolved within the vitrified mass, which has reached such a fluidity as to allow the gas to blow a spherical pore. The pore now acts as a gas container. These vesicles cannot be formed unless the vitrified mass possesses sufficient fluidity. The vitrification is controlled to some degree by the nature of the mixing of the raw clay and grog. Maybe this mixing plays some considerable part in the apparent extent of the vitrification of the Scottish material.

The differences between the true porosities of the interior and exterior illustrate the physical heterogeneity of the material during firing. The constitutional heterogeneity will be indicated

in the consideration of the colour changes. The Stourbridge material appears to be more homogeneous in structure than the Scottish. Even here, however, the interior and exterior porosities differ by over 1·07 at the finishing temperature.

In the case of Series A and Series G the porosity increases during the cooling period. This may be due to crystallization of certain mineral constituents and to the contraction of the matrix.

Loss on Ignition.

The results concerning the "loss on ignition" data reported in this paper were obtained by the usual method of igniting a weighed quantity of the dry powdered material in a porcelain crucible, with a finishing temperature of upwards of 1,000°C.

Houldsworth and Cobb[13], in their valuable contribution on "The Behaviour of Fireclays, Bauxites, etc., on Heating," determined the progressive loss in weight which samples of their materials underwent during a heating from 15°-1,000°C. over a period of two or three weeks. This work led these authors to the interesting conclusion that the dehydration of clay substance does not take place in stages, but is effected between 420°-450° on prolonged heating. Further, they state that with kaolin, it is possible that the loss in weight from 450°-1,000° might have been brought about by continuing the heating at 450°, but that an extremely lengthy period of time (running into months) would be necessary for the purpose. A similar result was obtained with a sample of Farnley fireclay.

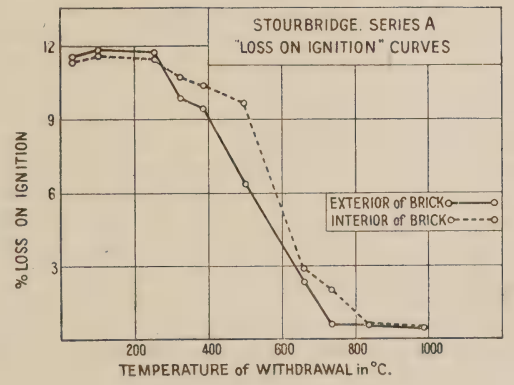


Fig. 8.

Consider Figs. 8 and 9, which show the decrease in the value of the loss on ignition of samples of Stourbridge and Scottish material with the increase in the temperature of withdrawal. With the Stourbridge product, the decrease at 320° corresponds to the increase in specific gravity and porosity noted at this temperature.

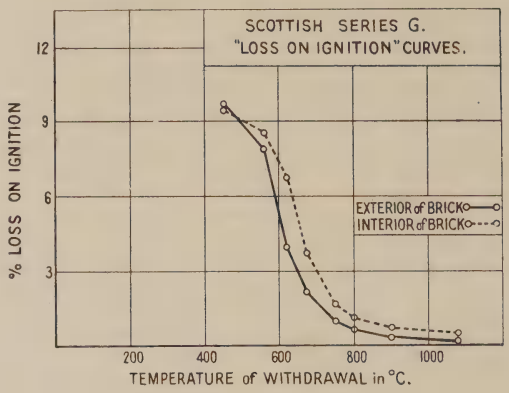


Fig. 9.

It is very probably concerned with the decomposition of bituminous matter. The rate of decrease becomes very pronounced at 450°-500°, the loss on ignition of the exterior portion being reduced by 45%. It would seem, then, that these results are in keeping with those reported by Houldsworth and Cobb. However, the temperature measurements cannot be relied on with any degree of certainty, although there can be little doubt that a considerable dehydration of kaolinite has taken place before 520° was reached.

It will thus be appreciated that the concentration of water vapour in the kiln atmosphere continues to a very great extent from ordinary temperatures up to, at least, 700° and that for the oxidation period to be very effective the utmost endeavour has to be made to remove the water before the temperature reaches approximately 800°. In the Stourbridge continuous kiln this removal seems to proceed continuously adding effectively to the rapid elimination of the black core, which is noted later.

The results for the Scottish material do not indicate such an early breakdown of the clay substance, although there are definite indications that the dehydration has commenced at 500°. The inaccuracy of the temperature measurements, again vitiate an uncompromising comparison.

A rough approximation based on a study of the nature of these "loss on ignition" curves suggests that there was a gradient of about 50°C. between the exterior and interior of the brick at 600° during firing. This fact, may have been suggested[1] from the previous work of the authors on temperature gradients , since it agrees with the kiln rate of heating of about 15° per hour.

CONTRACTION.

The dimensions of all the sample bricks were obtained and the volume of each sample computed. The shrinkage in volume was

then deduced. The results are not at all good, particularly those obtained for the Scottish material for temperatures between 600° and 900°C. (*vide* Fig. 10), although they allow of certain conclusions. Considering the accuracy required for indisputable comparisons the method of measuring samples so drawn from a kiln and transported cannot but be regarded as very approximate. Consequently, the results are only used to substantiate conclusions drawn from other data.

The accurate measurements of contraction due to heat treatment at high temperatures is certainly an indication of the progress of vitrification, and has often been used for such purposes. In fact Mellor,[14] who has drawn many interesting conclusions from the use of this method, states that the outward and visible sign of the work done by the heat is the contraction.

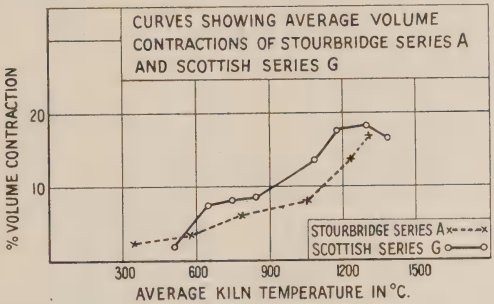


Fig. 10.

Fig. 10 is a curve constructed from the data of contraction for the Series A and the Series G. The temperature indicating the commencement of the vitrification seems to be considerably lower in the case of the Scottish product, a fact which was indicated by the other data. Further, the contraction, and, consequently, the speed of vitrification (if the assumption of a direct proportionality between the two, be allowed), continues with the Stourbridge material, but slackens off considerably with the Scottish product. It seems, therefore, that the Scottish product "matures" first. It is worthy of mention that Series A.G. and Series P also show this decrease in the contraction rate during the last phases of the burning. Thus, although the finishing temperatures are practically the same in the case of Series A and Series P, the effects of vitrification are more pronounced in the latter series. This may be due, either to conditions of time or of kiln atmosphere. Most likely it is a combination of both circumstances.

General Discussion.

"Water-Smoking."

The water-smoking period has received previous experimental onsideration from the authors[1]. As the result of this work they suggested that 28 hours would serve adequately to allow the brick

to reach 250° without causing undue strain within the material in the circumstances of their experiments, which, probably, included the prompt removal of water-vapour from the atmosphere. In this connection, it is interesting to note that 24 hours were taken approximately to reach this temperature in the actual continuous kiln firing. This result indicates very satisfactory conditions, both with regard to the removal of water-vapour and the careful control of rate of rise of temperature. In the round kiln, however, owing to certain causes inherent in the nature of the kiln construction and manipulation, including the great difficulties encountered in removing the water-vapour from the kiln atmosphere, 96 hours were required to reach 250°.

The estimated time required for the water-smoking of the Scottish products, G. and A.G. up to 250° are 10½ and 12½ hours respectively. In the work to which reference has already been made, it was suggested that the time to reach 250° should be about 17 hours.

The Elimination of Carbonaceous Matter.

Table V. shows very definitely that approximately 72 hours elapse in the heating of the Stourbridge product in the continuous kiln before the whole of the carbonaceous matter is eliminated. Further, the time taken to progress from the commencement of apparent oxidation (5A) to its complete removal (9A) is 32 hours. In the firing of this series, an approximation to muffle conditions was probably obtained. Thus, a direct comparison may be made between these times and those quoted in another paper by the present authors (Observations on the Elimination of Carbonaceous Matter from Fireclay Bricks)[15] particularly concerned with the experimental elimination of the carbonaceous matter in this same Stourbridge product. In the first place it may be mentioned that the temperature 390°, given in connection with Sample 5A, is very much lower than that noted in experiments by the present authors, for a similar effect. This temperature obtained by experiment was between 500°. Again, with the half-brick it has been shown that after allowing 2·5 hours to progress from nearly 550°-650°, a period of nearly 24 hours at 650° is necessary to remove all the carbonaceous matter. During the removal in kiln firing the temperature rises much above 650° and the speed of removal at these higher temperatures will be increased. However, this increase in speed will not be so great as might be at first expected, since the major factor must be the speed of ingress of oxygen into the brick. Such a factor is controlled amongst other conditions by (1) the composition of the kiln atmosphere ; (2) the nature and extent of the porosity, *i.e.*, capillaries in the clay; (3) the nature and "buffer" effect of the gases formed, and partially remaining in the brick. Since the experiments on the half-brick indicate that from 36-40 hours at 650° will be necessary for the removal of the carbonaceous matter from the full-sized brick, the

complete removal taking place in 32 hours in the kiln firing shows very good manipulation. These facts go to prove also that there is a very successful removal of water-vapour from the kiln atmosphere and further, that the oxidizing conditions at the proper time, are well maintained.

The data of the firing of the Stourbridge product in the round kiln show that approximately 180 hours elapse before the removal of the carbonaceous matter is evident and that 52 hours are necessary to complete the change from the first indications of oxidation to the final elimination of the core. This is, well in excess of the time required in the continuous kiln. In the case of the Scottish material, the bricks are in the kiln 55-62 hours before the black core is removed; also, approximately 40 hours are required to progress from the commencement of oxidation to the final elimination of the carbonaceous matter. Since there is less carbonaceous matter in this product than in the Stourbridge material, and further since it is not of the same bituminous nature, it can be seen, from the samples, that the manufacturer does no consider its removal a great difficulty. This fact is well indicated by the samples withdrawn at temperatures of over 1,000°C. They show faint indications of a "black core," which, however, does not persist. Further experiements on the firing of the Scottish material have shown that the carbonaceous matter is completely removed when the time taken to raise the temperature of the kiln (containing 600 bricks) from 500°C. to 1000°C. is not more than 20 hours.

An interesting feature is the development in samples 8A and 20P, *of a white to bluish white border surrounding the carbonaceous matter.* This development has been noted in experimental work by the present authors reported elsewhere. It seems to be formed at temperatures over 600°C. and to mark the last stage in the elimination of the core. From a visual examination, it is certainly outstanding, but its exact significance is not known. The yellowish white core which results after the elimination of the carbonaceous matter is characteristic where the temperature exceeds 600° and shows up in contrast to the pink border layer. These interior tinctorial effects are in all probability the result of the atmosphere inside the brick, which must be very reducing during the removal of the carbonaceous matter.

The Formation of "Iron" Specks and Patches.

The formation of "iron" specks, patches, etc., is of some considerable technical interest. With the Stourbridge product, fired in the continuous kiln these specks are not noted except in the final specimen which is withdrawn during the cooling period. With the round kiln product, however, they can be distinguished in sample No. 24P, the temperature of withdrawal of which is given as 1,015°. With the Scottish product, Series A.G. they appear in sample 11 A.G. at a given temperature of 1,130°C. While with the Series G, sample 8G the temperature of which is reported as 1,075° shows them for the first time. It is of excep-

tional interest then, to note that in the kiln firing where the conditions approximate to those of a muffle these specks do not appear during the firing, whereas in other atmospheres they show up roughly at temperatures of about 1,050°C. Some investigators have suggested that these specks are due to the decomposition of ferrous sulphide, in the neighbourhood of 950°, with the subsequent formation of a fusible ferrous silicate. The sulphide, although it is often present in the original clay material, is, according to Jackson[16], in the main a direct result of the action of sulphurous gases on the impurities in the clay. He states that iron oxide impurity in the clay is eager to absorb sulphur from any source while being heated to 680°. Since there is iron in clay and sulphur in the fuel there will be an absorption of sulphur by the ware. The sulphur must be burned out at low temperature, and hence there should be a delay in burning owing to this cause. From a study of analytical work on the sulphur products formed in the clay, Jackson postulates the existence of a ferrous sulpho-silicate, which is not decomposed until a temperature of approximately 750° is reached. The existence of this compound as preliminary to the formation of the noted "iron" specks seems very feasible.

The cause of the very few "iron" specks noted in the cooling period sample of Series A seems to be of a different nature.

Colour.

A study of the variations of colour suggests that the samples can be roughly placed in five categories: (1) Samples withdrawn at temperatures below 500°. In these there is no marked change in colour; (2) Samples withdrawn at temperatures between 500° and 900°. The exterior colour of these samples is pink or pinkish-white, while the interior, at the lower temperatures shows the black core, and at the higher temperatures, a yellowish-white or greyish-white colouration; (3) Samples withdrawn at approximately 1,050°C. The predominant colour of the interior and exterior portions of these specimens is either a yellowish-white or a greenish-white; (4) Samples withdrawn at temperatures over 1,100°. In this category, many shades of brown, ranging from "dirty" yellowish-brown to reddish brown make their appearance either in localised patches or diffused throughout the mass in varying shades; (5) Samples withdrawn during the cooling period. Here the colour, varying from red to brown, is particularly "clean," and its effect is homogeneous throughout the mass.

The colour changes in fireclays due in the main to iron and calcium compounds have been discussed by a number of investigators, chiefly including Seger[17] and Orton[18].

The present work shows up well the bleaching effect noted in the region of 1,050°. This change starts shortly after vitrification, and is probably connected with the formation of complex silicates perhaps a yellow ferrous calcium silicate. However, it must be emphasized that this very pronounced change took place in all the investigated series. The other change of very marked effect takes

place during the cooling period and consists essentially of a particularly significant alteration to a clean reddish-brown or red colouration which permeates the whole brick. The specific gravity data have indicated a possible constitutional change, and the change in the appearance of the specimens certainly upholds this. Further, there appeared to be a much greater constitutional homogeneity, in these samples, than has hitherto existed during the burning, a fact which is also upheld by the specific gravity data. A full discussion of the colour effects will appear in a later paper, in which results obtained in the firing experiments under industrial conditions together with work herein reported will be embodied.

TABLE 9.

THE CONSIDERATION OF TIME FACTOR.

Nature of Heat Work.	Stourbridge Product		Scottish Product	
	Continuous Coal-fired Kiln. Series A.	Round Kiln. Series P.	Continuous Gas-fired Kiln. Series G.	Continuous Gas-fired Kiln. Series A.G.
Total time required to finish firing (not including cooling period) in hours.	104	248	92	105½
Water-smoking period (*i.e.*, time taken to reach 250°) in hours.	24	96	10½ (approx.)	12½ (approx.)
Time required to eliminate carbonaceous matter (*i.e.*, from the commencement of oxidation to the final disappearance of the core) in hours.	32	56	36–40	36–40
Time during which the water of constitution of the clay substance is being evolved in hrs.	24	40	30	—
Time during which vitrification is continuing in hours.	28	70	37	45

Table 9 shows at a glance the approximate times required to complete the various kinds of heat work in the kiln. The contrast between the round kiln and the continuous kiln data is very marked. The economies of the continuous kiln are made easily apparent, when one realizes that the product is in every way as good as that obtained from the round kiln.

The water-smoking times have been discussed earlier in the paper, also, it has been indicated that the time taken to eliminate the carbonaceous matter in the case of Series A agrees well with that obtained in an experimental muffle. The time taken for this

work in the case of the Scottish material seems to be slightly longer. The explanation of this may be in the fact that, although there is only a small amount of carbonaceous matter present, the vitrification range is reached before all the carbon is eliminated, and this considerably increases the time.

The duration of the elimination of the water of constitution is obtained mainly from loss on ignition data. These data seem to show that there will be an excessive concentration of water-vapour in the kiln atmosphere for, at least, 65% of the time of firing.

The period of vitrification is a topic on which considerable argument has been extended. In the present examples, it is interesting to note that, with the shortest period of vitrification (Series A), the data of specific gravity and porosity point to the fact that the maximum speed of vitrification was in progress when the firing was stopped. In the case of the Scottish material, however, this maximum speed was passed some considerable time before the firing was finished. The extra heat work here, may have had the effect of dissolving constituent in the fusing matrix, which gives rise to other crystallizations during cooling. However, Dr. Mellor[19] has already pointed out that there is apparently a satisfactory finishing temperature for most clay products, and to exceed such a temperature adds nothing to the properties of the final product but may detract from them. How far this is the case with Series G and Series A.G. must be determined in the actual firing research. Also, such work, alone, will prove whether increasing the heat work on Series A will improve the product.

Summary.

(1) Samples of firebricks have been withdrawn from four kilns at various stages during the firing, and data concerning them have been determined in the laboratory.

(2) The true specific gravity data indicate chiefly (*a*) the change in the kaolinite molecule progressing from about 450° to 570°; (*b*) the polymerization of the alumina molecule about 950°, and (*c*) some considerations respecting the vitrification range.

(3) The range of maximum porosity and the other facts concerning the vitrification range are shown by the true and apparent porosity determinations.

(4) The "loss on ignition" data give an indication of the commencement of the dehydration of the kaolinite and allows a time-factor during which water-vapour is being evolved from the clay substance, to be obtained.

(5) The determinations of volume contraction, though necessarily inaccurate, substantiate the conclusions appertaining to the vitrification range, based on the specific gravity and porosity data.

(6) Visual observation of the specimens gives valuable information concerning (*a*) the elimination of carbonaceous matter; (*b*) the appearance of "iron" specks and blotches; (*c*) the colour changes taking place during burning, and (*d*) the vitrification of the products.

(7) The data of water-smoking agree with those formulated from a previous laboratory experimentation.

(8) A consideration of the times factors required for doing the necessary heat-work in the kilns is appended.

In conclusion the authors wish to thank Mr. H. Edwards of the Pottery Laboratory for continued help during the progress of the work.

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Results, as shown in Tables 1, 2—8, follow.

TABLE I.

DATA OF SERIES A (STOURBRIDGE PRODUCT: CONTINUOUS KILN).

Mark.	Temp. of Withdrawal. °C.	Hours of Firing.	% Vol. Contraction.	True Specific Gravity.			True Percentage Porosity.			App. Percentage Porosity.		
				Exterior	Interior	Average	Exterior	Interior	Average	Exterior	Interior	Average
1A	30	8	—	2·605	2·605	2·605	25·7	25·8	25·7	22·5	22·2	22·3
2A	100	16	—	2·604	2·608	2·606	25·6	25·7	25·6	22·2	22·4	22·3
3A	250	24	—	2·604	2·616	2·610	25·9	25·4	25·7	23·5	22·9	23·2
4A	320	32	0·57	2·636	2·611	2·624	26·0	25·1	25·6	25·2	24·3	24·8
5A	390	40	3·87	2·634	2·601	2·618	26·7	25·9	26·3	26·0	25·9	26·0
6A	500	48	2·73	2·576	2·572	2·574	27·5	26·7	27·1	27·9	26·8	27·3
7A	650	56	4·24	2·579	2·545	2·561	31·2	31·3	31·3	30·4	30·1	30·2
8A	730	64	5·66	2·622	2·595	2·608	33·2	32·4	32·8	32·7	31·1	31·9
9A	825	72	6·22	2·674	2·667	2·670	33·5	34·0	33·7	33·7	33·4	33·5
10A	990	80	6·50	2·677	2·671	2·674	33·6	33·9	33·7	33·1	33·6	33·4
11A	1110	88	9·71	2·665	2·658	2·662	31·1	32·2	31·7	30·0	31·6	30·8
12A	1220	96	13·7	2·673	2·675	2·674	27·4	29·3	26·4	26·3	28·3	27·4
13A	1300	104	16·6	2·617	2·645	2·631	22·6	23·8	23·1	23·1	24·2	23·6
14A	?	104+ cooling period	16·7	2·638	2·657	2·648	23·7	25·5	24·6	23·2	25·2	24·2

TABLE 2.

DATA OF SERIES P (STOURBRIDGE PRODUCT: ROUND KILN).

Mark.	Temp. of Withdrawal. °C.	Hours of Firing.	% Vol. contraction.	True Specific Gravity.			True Percentage Porosity.			App. Percentage Porosity.		
				Exterior	Interior	Average	Exterior	Interior	Average	Exterior	Interior	Average
6P	120	48	—	2·594	2·614	2·604	—	—	—	—	—	—
8P	165	64	—	2·602	2·612	2·607	25·3	25·7	25·5	21·3	20·9	21·1
11P	240	88	—	2·614	2·612	2·613	26·0	26·3	26·1	22·3	21·7	22·0
14P	400	112	3·01	2·626	2·619	2·622	26·1	26·1	26·1	23·1	23·5	23·3
16P	570	128	3·95	2·643	2·622	2·632	27·4	27·4	27·4	25·4	25·7	25·7
18P	800	144	3·85	2·572	2·577	2·575	29·8	29·3	29·5	28·4	26·2	27·3
20P	910	160	4·32	2·579	2·550	2·565	32·3	31·8	32·1	30·8	31·3	31·1
22P	965	176	8·55	2·664	2·662	2·663	31·1	32·2	31·7	30·2	31·6	30·9
26P	1080	208	15·1	2·666	2·672	2·669	27·6	29·3	28·4	26·5	28·1	27·3
28P	1245	224	13·9	2·664	2·669	2·667	27·2	29·8	28·5	25·3	27·2	26·1
30P	1305	240	15·8	2·660	2·662	2·661	26·7	27·7	27·2	25·0	26·3	25·6
32P	?	248+ 8 hours cooling.	16·4	2·669	2·668	2·669	26·3	28·6	27·5	24·3	26·8	25·6

TABLE 3.

DATA OF SERIES G (SCOTTISH PRODUCT: CONTINUOUS KILN).

Mark.	Temp. of With-drawal. °C.	Hours of Firing.	% Vol. Contr-action.	True Specific Gravity.			True Percentage porosity.			App. Percentage Porosity.		
				Exterior	Interior	Average	Exterior	Interior	Average	Exterior	Interior	Average
1G	450	14·5	1·94	2·668	2·671	2·670	25·2	26·2	25·7	23·0	24·2	23·6
2G	560	24·5	—	2·639	2·653	2·646	25·7	27·2	26·5	24·7	25·9	25·3
3G	620	29·5	5·65	2·596	2·630	2·613	27·2	27·9	27·6	26·3	26·6	26·5
4G	670	34·5	8·98	2·585	2·572	2·578	28·6	29·4	29·0	27·3	28·2	27·8
5G	730	39·5	7·67	2·596	2·593	2·594	30·0	30·3	30·1	28·6	29·0	28·8
6G	800	44·5	8·52	2·602	2·588	2·595	30·4	31·4	30·9	29·1	29·7	29·4
7G	910	49·5	8·67	2·624	2·619	2·622	32·6	31·2	31·9	31·7	30·3	31·0
8G	1075	54·5	11·7	2·637	2·624	2·629	29·1	30·4	29·8	28·4	29·6	29·0
9G	1085	59·5	15·0	2·664	2·638	2·651	26·3	27·7	27·0	24·1	24·9	24·5
10G	1160	64·5	17·0	2·657	2·637	2·647	26·5	26·9	26·7	23·9	24·3	24·1
11G	1210	69·5	17·4	2·646	2·619	2·633	27·1	27·0	27·0	23·2	23·5	23·4
12G	1375	74·5	18·4	2·641	2·617	2·629	24·9	26·8	25·8	20·5	22·6	21·5
13G	1240	79·5	17·7	—	—	—	—	—	—	20·4	22·1	21·3
14G	1310	84·5	17·6	2·637	2·628	2·633	24·7	25·3	25·0	19·8	20·3	20·0
15G	1410	89·5	17·1	2·657	—	—	25·8	—	—	19·8	21·8	20·8
16G	1480	92·0	15·6	2·643	2·622	2·633	25·7	27·1	26·3	21·0	19·2	20·1
17G	?	with-drawn during cooling.	17·2	2·657	2·658	2·658	24·5	27·8	26·2	20·1	22·1	21·1

TABLE 4.

DATA OF "LOSS ON IGNITION".

Stourbridge Product ; Series A.				Stourbridge Product ; Series P.				Scottish Product ; Series G.			
Mark.	Temp. of With-drawal in °C.	Loss on Ignition.		Mark.	Temp. of With-drawal in °C.	Loss on Ignition		Mark.	Temp. of With-drawal in °C.	Loss on Ignition.	
		Exter-ior.	Inter-ior.			Exter-ior.	Inter-ior.			Exter-ior.	Inter-ior.
1A	30	11·56	11·34	1–10P	30–240	11·82	11·64	—			
2A	100	11·82	11·46	11P	240	11·90	11·60	—			
3A	250	11·68	11·54	12P	250	11·75	11·60	—			
4A	320	9·88	10·70	13P	—	—	—	—			
5A	390	9·44	10·26	14P	400	11·10	11·10	—			
6A	500	6·22	9·52	15P	460	9·58	10·70	1G	450	9·74	9·44
7A	650	2·46	2·86	16P	570	9·24	10·0	2G	560	7·90	8·46
8A	730	0·56	1·86	17P	650	8·80	9·90	3G	620	4·00	6·84
9A	825	0·50	0·52	18P	800	7·10	8·88	4G	670	2·14	3·72
10A	990	0·34	0·36	19P	870	3·70	7·04	5G	730	1·04	1·60
—	—	—	—	20P	910	1·84	2·20	6G	800	0·64	1·14
—	—	—	—	21P	940	0·40	0·50	7G	910	0·22	0·66
—	—	—	—	22P	965	0·25	0·20	8G	1075	0·10	0·54

General Appearance and Colour of Specimens.
Table 5.
Stourbridge Product; Series A, Continuous Kiln.

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
1A	30	8	Dark grey colour.	Dark grey colour (similar to Series P, 1–14P).
2A	100	16	Same as 1A.	Same as 1A.
3A	250	24	Slightly darker grey than 2A, probably due to the deposition of carbonaceous matter from kiln fuel.	Similar to 1A.
4A	320	32	Slightly lighter than 2A, suggesting the commencement of the breakdown of the carbonaceous matter of the clay.	The change from the unburned appearance starts here. There appears to be a slight decomposition of the carbonaceous matter to the depth of about 1 cm. A dirty pink border layer, very indefinite in contour makes its appearance.
5A	390	40	This surface is markedly lighter with a dirty whitish pink shade.	The "carbon" core is definitely indicated. This core measures approximately 8·8 ×4 cms. The border is about 1·2 cms. in thickness and is "sandy" in colour.
6A	500	48	Similar to 5A. The colour is cleaner with the pink tinge more pronounced.	The core, which is sharply defined, measure 8×3·5 cms., it is *darker* in appearance, the border layer is about 1·4 cms. in thickness and possesses a slightly dirty salmon pink colour. The extreme edge of the core is slightly lighter.

TABLE 5.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
7A	650	56	The colour is still lighter with the pink tinge even more pronounced.	The core, which measures 7·7 × 3 cms. appears to be slightly darker than in 6A. There is a suggestion of a white line surrounding the black core. The border layer, which is 1·8 cms. in thickness, is a deeper salmon pink in colour.
8A	730	64	Similar to 7A.	The core measures 7·3 × 2·8 cms. and has changed in colour to a bluish or grey-black colour. *This core is surrounded by a white layer about* 0·3 *cms. in thickness.* The actual border layer has a lighter salmon pink colour than in 7A, and is about 2·0 cms. in thickness. This specimen marks the final stage in the elimination of the black core.
9A	825	72	A pinkish white colour, cleaner than previous specimens.	The border layer is a much lighter pink and is very clean. *The black core has now been replaced by a yellowish white area measuring* 7·2 × 3·8 *cms. approx.*
10A	990	80	Much whiter than 7A, with the barest suggestion of a pink shade.	Similar to 9A, although the white area is not quite so clearly defined. There is a suggestion that the colour is beginning to even up.
11A	1110	88	Still very light in colour. The white colour is tinged in places with a yellowish-green shade.	The yellow white area has spread through the brick, making the colour of the whole section very even.

TABLE 5.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal n °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
12A	1220	96	There is here a marked change in the colour which is now deeper and of a greenish yellow shade.	The colour is deeper, homogeneous and of a lighter brownish yellow shade.
13A	1330	104	The colour is lighter, *i.e.*, a lighter brownish yellow.	The colour is lighter than 12A, being dirty white.
14A	?	104+ cooling for 8 hours.	This specimen shows a most marked change. The colour is a clean, bright brown.	Another sharp change resulting in the production of a bright brown colour, which is not so deep as in No. 32 of the Series P. A few "iron" specks can be distinguished in this section. This is the first time "iron" specks have been noted in this series.

TABLE 6.

STOURBRIDGE PRODUCT; SERIES P, ROUND KILN.

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
1P–13P	30–300	8–104	Surfaces covered by a layer of sooty, carbonaceous matter, which appears to increase in amount up to No. 14P. The colour of this layer changes very slightly at No. 11, showing a brownish shade.	No change from that of the unburned clay.
14P	400	112	As in 1P–13P.	First perceptible change in colour. Very faint reddish tinge on dark grey ground.
15P	460	120	Carbonaceous layer still persists, but to a much less extent.	A rectangular core, measuring 9 × 4 cms., can just be distinguished. A change in the nature of the carbonaceous matter, with a consequent change in the colour can be detected to the depth of about 1 cm.
16P	570	128	Much cleaner surface, the colour of which is pinkish grey.	The black core measuring 9 × 3·4 cms. is much more pronounced in outline. A "sand" coloured border about 1·5 cms. in thickness surrounds the core.
17P	650	136	The surface shows a light salmon colour.	The black core measures 7·5 × 3 cm. The thickness of the border is about 2 cms., it is clean and lighter in colour and has a pinkish tinge.
18P	800	144	Somewhat dirtier in colour than No. 17P. This is no doubt due to the fuel used in kiln.	The core which measures 7·5 × 2·5 cms. appears to be darker and more defined. The border about 2·1 cms. in thickness is cleaner and deeper in colour.

TABLE 6.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
19P	870	152	Brighter and cleaner, possessing a salmon coloured shade.	The black core which appears to be still darker measures 7 × 2·5 cms. The pinkish border which is more defined and cleaner is about 2 cms. in thickness.
20P	910	160	Generally the colour is brighter than in No. 17P, although there are patches covered with carbonaceous matter from the kiln fuel.	*The black core measuring* 7 × 2·5 cms. is *surrounded for the first time, by a white layer about* 2 *mm. in thickness.* The outer border which has a thickness varying from 1·5–2·0 cms. has a light salmon shade.
21P	940	168	The colour has now definitely changed to a dirty greenish white.	This cross section shows a startling change. The core measuring 5 × 2 cms. is light bluish grey, which grades to a dirty white and then yellowish white for the border layer.
22P	965	176	Practically the same as 21P, perhaps slightly deeper in shade.	The core has practically disappeared. This section shows a yellowish-white colour.
23P	985	184	Definite change in colour to a light reddish brown.	Major portion of section light dirty yellow.
24P	1015	192	Much deeper colour than 23P Black "iron" specks—small pinholes—appear for the first time.	Khaki area in the centre, shading off to a dirty yellowish brown at the edge.
25P	1040	200	This surface shows a dirty greenish brown shade, together with an increase in the number of "iron" specks.	This section shows a greenish brown colour, with a pronounced greenish effect towards the centre. "Iron" specks appear in the interior for the first time.

TABLE 6.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
26P	1080	208	Darker in shade than 25P. "Iron" specks increase in size and quantity and continue to do so in the following specimens of this series.	Generally darker than 25P. A lighter core with a dirty greenish tinge can be traced. "Iron" specks increase in size and quantity and continue to do so in remaining specimens.
27P	1175	216	Dirty reddish brown in colour.	This section is a slightly darker brown in colour.
28P	1245	224	Similar to 27 the "iron" has formed "pits" in the surface.	Colour slightly darker than 27P with the merest suggestion of a lighter core.
29P	1280	232	Similar to 28P, but tinged with a reddish shade.	Slightly dirtier than 28.
30P	1305	240	Reddish brown mottled with "iron" pits, patches and specks.	Pronounced change in the colour of the border layer to a clean reddish brown to the depth of 2 cm. The interior colour—greyish brown—is similar to the general colour of 29P.
31P	1325	248	Darker than 30P, otherwise similar.	The greyish brown interior is barely suggested. The border colour of 30P covers nearly the whole section.
32P	?	248+8 hours cooling in kiln.	This surface shows a very definite change to a brownish red colour. A mottled effect is created by the predominance of "iron" specks.	The surface colours prevail throughout the section. Except for the "iron" patches, this colour is homogeneous throughout.

TABLE 7.

SCOTTISH PRODUCT: SERIES A.G.

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
1A.G.	450	17	Dirty grey or stone colour.	The colour on three borders to a thickness of 0·3 cms. is slightly lighter than the remainder.
2A.G.	510	22	As in 1A.G.	Practically as in 1A.G.
3A.G.	585	27	Slightly lighter in colour.	The border layer which still has a thickness of about 0·3 cms. is lighter in colour and forms a sharper boundary. The interior shows no apparent change.
4A.G.	625	33	The colour which is decidedly lighter than 3G, is a very light grey.	The border layer which is now 0·5 cms. in thickness is much whiter than in 3A.G. The core is darker in colour.
5A.G.	690	37	Practically as in 4A.G.	Practically as in 4A.G. except that the core appears to be of a darker shade.
6A.G.	810	42	Ditto.	Ditto.
7A.G.	810	47	The surface is cleaner, in fact it is practically white.	Ditto.
8A.G.	860	52	Ditto.	Ditto.
9A.G.	950–1000	57	The surface material is mechanically stronger c.f.1A.G.–8A.G. are fragile. The colour is a very clean white.	A sharp change is here noted. The core is much lighter and less sharply defined. There is a grading of shade from the edge to the core.

TABLE 7.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
10A.G.	1075	62	The surface is a clean white with a slight pink tinge.	The section is homogeneous in colour, *i.e.*, white with a suggestion of pink. The core has entirely disappeared.
11A.G.	1130	67	Change in colour to a yellowish white with very light greenish patches. "Iron" specks first appear here and continue to grow in size and in number in the following specimens.	The appearance is homogeneous except that the grog here begins to show up well. The colour is a dirty yellowish white. There is no suggestion of a core.
12A G.	1210	72	A very light yellowish brown, mottled owing to the presence of iron specks.	Here is noted the definite appearance of a mottled brownish irregular stain in the interior of the section, which contrasts sharply with the whitish border. There is a deepening of the colour of this stain towards the centre. The grog shows up as whitish specks.
13A.G.	1350	77	Slightly darker due to more mottled appearance.	The interior stain is still pronounced. The brown colour on the exterior of the stain changes to a dirty grey in the interior. The grog is very distinct.
14A.G.	1360	82	Darker than 13A.G. "Iron" specks more pronounced and the surface is more mottled.	As in 13A.G.
15A.G.	1350	87	As in 14A.G.	As in 13A.G.
16A.G.	1400	92	Slightly browner in general appearance.	The interior stain is much less in evidence. This section shows a more homogeneous dirty brown colour with white specks of grog standing out in relief.

TABLE 7.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
17A.G.	1430	97	As in 16A.G.	As in 16A.G.
18A.G.	1430	102	The same mottled appearance in which the predominant colour is a greyish brown.	This section of the brick is cleaner.
19A.G.	1450	105½	No change.	No change.
20A.G.	?	Taken out during cooling of kiln.	A great change is noted. The colour is a light reddish brown, mottled with darker brown spots and patches.	The general colour is a clean light reddish brown as on the surface. There are in a few darker brown spots due to "iron." The grog is distinct showing up as small white areas.

TABLE 8.

SCOTTISH PRODUCT; SERIES G, CONTINUOUS KILN.

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
1G	450	14·5	Uniform dirty grey or stone colour.	Uniform slate grey in appearance.
2G	560	24·5	Slightly lighter in colour.	A dirty whitish border layer 0·5 cm. in thickness surrounds this section.
3G	620	29·5	Change in colour to a dirty greyish white.	The border layer in this section is more sharply defined. The interior is darker in colour, approximating to a bluish black.
4G	670	34·5	Ligher in shade than in 3G.	Similar to 3G, except that the interior seems to be darker.
5G	730	39·5	Still lighter in shade with a very faint pink tinge.	The border boundary is not so well defined. The interior continues to become darker.
6G	800	44·5	Very light shade almost white.	The border has lost its pinkish tinge. It is not sharply defined and the interior is much lighter.
7G	910	49·5	As in 6G.	The border layer now extends to a depth of 2–2·5 cms. The interior is a light slate grey.
8G	1075	54·5	The colour is white with a suggestion of yellow. A few "iron" specks appear for the first time.	The border is not so pronounced and merges into a much lighter interior.
9G	1095	59·5	There is here a distinct change in colour to a dirty brownish yellow. Numerous "iron" specks are noted.	The border is a brownish yellow layer about 1·5 cm. in thickness, it merges into a light grey interior.

TABLE 8.—(*Continued*).

Mark.	Approx. Temp. of Withdrawal in °C.	Hours of Firing.	Colour, etc., of Surface.	Colour, etc., of Interior.
10G	1160	64·5	The general colour is a dirty brownish yellow, darker in shade than 9G numerous "iron" specks and patches can be seen. The grog shows up distinctly as grey specks.	The border is browner than in 9G. The interior also shows a brownish shade.
11G	1210	69·5	The brown colour is much deeper. From now onwards the "iron" specks, patches and pits increase in size and quantity.	This section shows a mottled brown appearance with white specks of grog. There is a distinct suggestion of an inner greyish core.
12G	1375	74·5	The surface shows a distinct change in colour to a stone grey shade with a dappled effect due to brown' 'iron" specks and white particles of grog	A mottled brown appearance.
13G	1240	79·5	Similar to 12G with a brownish tinge.	The whole appears to be slightly darker with a suggestion of a border layer darker than the interior.
14G	1310	84·5	Similar to 13G	This section is darker than 13G with a suggestion of a grey interior.
15G	1410	89·5	Very brown and dappled appearance.	Similar to 14G.
16G	1480	92·0	A greyish brown shade with dappled appearance. Slightly lighter than 15G.	Similar to 15G although slightly lighter.
17G	?	Taken during cooling period	The surface is clean salmon brown colour, with large "iron" patches and the grog showing up as white areas.	Clean salmon brown colour with "iron" patches and white grog showing up. There is no suggestion of a core—a homogeneous effect throughout. This is a distinct and remarkable change. (cf. Series A, P and A.G.—Final Samples).

XV.—Observations on the Elimination of Carbonaceous Matter from Fireclay Bricks.*

By L. S. Theobald, B.Sc., A.R.C.S., and A. T. Green.

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Introduction.

The work which is described in this paper forms a part of the preliminary experiments which have been carried out in connection with the burning of fireclay bricks. A previous paper[1] has been written concerning the work done on the so-called "Water-Smoking" period, and the result of an examination of samples drawn at regular intervals during several complete burns of firebricks is given in a paper by the authors entitled "An Investigation of the Changes taking place during the Industrial Burning of Firebricks." The investigation now to be described is concerned with the removal by decomposition and oxidation of the carbonaceous matter which may be a cause of the unsightly "black cores"[2]—known to occur in certain types of fireclay bricks as a result of the poor firing conditions.

Speaking generally the scheme of work has been to heat portions of green bricks to temperatures up to 900°C. at various rates, maintaining the temperature constant, in many cases, for a definite period of time. The pieces were then broken across, their centres examined and the extent of any changes noted.

Materials used.

The materials have been of the same kind as those used in the study of the water smoking period mentioned above, but the majority of the runs have been made upon the Stourbridge fireclay as this seemed to show the elimination of the carbonaceous matter to the greatest advantage. (For details of analysis, etc., see previous paper, p. 105, also *Bull. B.R.R.A., No.* **8**, 1924).

Procedure.

The green bricks were allowed to dry in the air of the laboratory over a period of several months and were then sawn into eight parts, giving pieces of approximately the dimensions $3'' \times 2{\cdot}2'' \times 2''$, and this size was kept the same throughout the earlier portion of the work. Towards the end of the work, however, tests were carried out, in each case, on a half brick. Two were placed together in the centre of the muffle, and the rise in temperature was controlled by means of a platinum platinum-rhodium thermocouple and recording instrument. The type of muffle available did not allow the temperature control to be as accurate as could be desired, although it was sufficiently accurate when the nature and object of the trials are taken into consideration.

(1) L. S. Theobald and A. T. Green, p. 105; *Bull.* **8**, 1924.
(2) J. W. Mellor Trans. **16**, 259, 1917, and others.

RESULTS.

The object of these runs has been to study the best conditions for the elimination of carbonaceous matter and the relations of time and temperature in this connection, always keeping in mind the main end of the work, viz., the reduction in time taken to burn fireclay bricks.

The first step in the process was to find with a fair degree of accuracy, the temperature at which oxidation, as judged by the change in colour of the surface, appeared to commence. The following table shows some of the results obtained in this direction.

*TABLE I. (Stourbridge Material).

Laboratory Mark.	Heat Treatment	Remarks
*D*7 *D*8	0–400°C. in 6 hours.	Colour of exterior and interior unchanged, apparently the same as the unfired material.
*D*9 *D*10	0–500°C. in 8 hours.	Surface a lighter colour than that of the raw clay. No suggestion of a pink tinge. Colour of interior darker. Oxidation not commenced, although decomposition of carbonaceous matter appears to have started.
Da	0–550°C. in 8 hours.	Indication of surface oxidation.
Da'	0–550°C. (or 580°) in 7½ hours approx.	Surface very faintly pink. Interior dark grey and extending to within 2 mms. of the edge. Oxidation commenced.
*D*3 *D*4	0–600°C. in 4 hours.	Oxidation to depth 2mms. from surface.
*D*1 *D*2	0–600°C. in 8 hours.	Oxidation to depth of 5 mms. from surface. Increased oxidation with time (cf. *D*3 and *D*4).
*D*5 *D*6	0–600°C. in 12 hours.	Oxidation to greater extent than *D*4, or *D*1. Note :— D4 oxidation to depth 2 mm. *D*1 ,, ,, ,, 3–4 mms. *D*5 ,, ,, ,, 8–9 mms.

* In all these 0°C has been taken for convenience to signify the temperature of the laboratory.

It will be seen that under the particular conditions of the heat treatment which the pieces undergo, no change is apparent at temperatures below 500°C., but at 600°C. oxidation has, undoubtedly, commenced, whilst the temperatures 550-590°C. form the limits between which oxidation becomes noticeable.

Comparison between *D*3, *D*1 and *D*5 shows the effect of increased time with the same finishing temperature on the amount of oxidation. This point is further illustrated in Table II, which shows the gradual elimination of carbon as the piece concerned is kept at 600°C. for increasing periods of time.

TABLE II. (Stourbridge Material).
Showing progressive oxidation at 600° C.

Laboratory Mark	Heat Treatment	Remarks
Da	0–550°C. in 8 hours.	Indication of surface oxidation.
Db	0–590° or 600°C. in 8 hours Held at 600°C. for 2 hrs.	Oxidation well started to a depth of 1 cm. from surface. Black core. 4×3·5 sq. cm. in area.
Dc	0–600°C. in 8 hours and held at 600°C. for 3 hrs.	Oxidation increased. Black core 3·2×3·5 sq. cm. in area.
Dd	0–600°C. in 8 hours, held at 600°C. for 4 hours Cooled in muffle.	Area of black core 3×2·8 sq. cms.
Dq	0–600°C. in 8 hours. Cooling. 0–600° in 2 hours and held at 600°C. for 6 hrs.	Black core of circular cross section diam. 10 mms. Surrounded by very faint yellowish ring 2 mms. wide. Remainder of piece usual salmon pink.
Dr	Same as in *Dq*, but held at 600° for 8 hours instead of 6.	*Black core eliminated.* Faint suggestion of a yellowish area in centre of piece—about 12 mms. square.
Ds	Same as in *Dq*, but held at 600°C. for 10½ hours. Cooled in muffle.	No black core, yellowish area faintly suggested. In no case was area so sharp and distinct as in series to 750°C.

All three pieces *Db*, *Dc*, *Dd* were heated up at the same time to 600°C., and then withdrawn at the periods indicated. *Dd* however, was allowed to cool in the furnace.

As was noticed with the full sized bricks drawn from actual burns (see previous paper), the cores become distinctly darker and blacker as the time at 600°C. is increased (viz. from *Db* to *Dd*), indicating possibly that as heating continues further changes are taking place in the carbonaceous matter in the centre of the piece. No bluish white ring was noticed at this particular temperature (600°C.), although as soon as the temperature approaches 650°C., or over a white ring, which develops into a yellow area follows the removal of the carbonaceous matter.

Development of Yellow Cores.

The pieces marked *Dq*, *Dr* and *Ds* were treated similarly to *Dc*, *Dd*, etc., with still longer soakings at 600°C., and in *Dr* the carbon is all burnt out in a period of eight hours. Faint suggestions of the development of a yellowish area occurred in these last, *Dr* and *Ds*, and as their positions in the furnace suggested that possibly an increased temperature was the cause, the tests were repeated in order to see if this development of a yellowish area at 600°C. could be established. Accordingly, three pieces were heated together as before and held at 600°C. for 11 hours. In two out of the three pieces no suggestion of a yellowish area occupying the previous position of the carbon occurred—the pieces being pink throughout—whilst the third showed only a very faint suggestion of the same. This non-appearance was confirmed in a subsequent experiment. (See *E*9 and *E*10, Table IV).

In the next series to 750°C., the yellowish area was always quite distinct and hence it was concluded that above say, 600°C. some chemical action takes place in a deficiency of air in the interior of the piece, which is manifested as a yellowish area replacing the carbon.

Finally, two pieces (E9 and *E*10, Table IV.), were heated up to 600°C. in eight hours, kept at this temperature for six hours, so as to burn out most of the carbon (see *Dq* and *Dr*, Table II.), and finally taken up to 900°C. in another four hours. On breaking these pieces in two, no trace of a yellow core could be detected—the colour was of a uniform salmon pink throughout. This indicated strongly that it is the carbon present which causes the yellow area to appear in the centre of the pieces, possibly by reducing the iron to a condition in which it reacts at temperatures above 600°C. to give this tinctorial effect.

It is also interesting to note that the surface of all pieces fired within the range 0-900°C. in these trials showed clear oxidation to a depth of about one centimetre, this area being sharply defined and its pink colour being in all cases quite clear with no suggestion of the yellow colour, which marked the interior of the pieces.

Oxidation at a higher temperature, viz., 750°C. was next studied—see Table III. The pieces were heated up to 750°C. at the rate used in the previous series and maintained as before, at this temperature for varying periods of time.

As was previously pointed out, there is again a darkening in the shade of the interior as if a diffusion of carbon had taken place. Reduction of the iron to the ferrous state may also contribute to this change.

The black cores at this temperature are definitely replaced by persistent yellow areas and a few tests were made to find out whether a more prolonged soaking at 750°C. would remove them. Pieces were heated as described under *Dh* (Table III.), and then soaked at this temperature for 9, 11 and 13 hours respectively,

TABLE III. (Stourbridge Material).

Showing progressive oxidation at 750°C.

Laboratory Mark	Heat Treatment	Remarks
De	0–750°C. in 10 hours	Black core 3·5 × 3·5 cms. surrounded by thin white line. Remainder salmon pink for depth of 1 cm. from the surface.
Df	0–750°C. in 10 hours and holding at 750°C. for 2 hours.	Black core—eliptical, 2·5 × 1·5 cm. surrounded by white area 0·5 cms. wide. Remainder salmon pink.
Dg	0–750°C. in 10 hours holding at 750°C. for 3 hrs.	Black core 2 × 2 cms. Whitish area as in *Df* 0·7 cms. wide. Remainder salmon pink. *Note.* 1. *Da* (Table I.), *De*, *Df* and *Dg* all heated in the one run. 2. Cores appeared darker than in *Da'*.
Dh	0–750°C. in 10 hours. Cooling. 0–750 in 2½ hours and holding at 750°C. for 3 hours.	All pieces oxidised to a pink colour at the surface and to fair distance internally. Yellowish white area in centre of pieces. Faint suggestions of black core.
Di	Same as in *Dh*, but held at 750°C. for 5 hours.	No black cores, all replaced by these yellowish white areas. Oxidation greater than in *E*5.
Dj	Same as in *Dh*, but held at 750°C. for 7 hours. Cooling in muffle.	No black cores, all replaced by these yellowish white areas. Oxidation greater than in *E*5.

but the yellow cores still remained. One piece in which this area had developed was heated in the Hirsch furnace, specially adapted for work on atmospheres, to 1,390-1,410°C. for two hours, in an atmosphere of oxygen. The yellow core did not disappear—on the contrary the salmon pink oxidised edges of the piece changed in colour, the piece itself showing a deepening of colour to a fairly uniform yellowish green.

The next range to be studied was from 0-900°C. at which temperature it is generally considered, and indeed as the previous paper shows for these materials vitrification commences. Table IV. shows the results which have been obtained for this range.

Tests were then being carried out with pieces of a larger size, but before describing these it may be as well to summarise the results which have so far been obtained.

TABLE IV. (Stourbridge Material).
Showing progressive oxidation at 900°C.

Laboratory Mark	Heat Treatment	Remarks
*E*1 *E*2	0–900°C. in 12 hours.	Black core 2 cms. square in centre of piece, surounded by bluish white ring 2 mms. wide. Surface pink and somewhat friable. Oxidation to a depth of 1·0-1·2 cms.
*E*3	0–900°C. approx. in 12 hours.	Black core 3·2 × 2·5 cms. White ring 1–2 mms. Remainder salmon pink. 1·1 cms. wide.
*E*4	0–900°C. in 12 hours at 900°C. for 1 hour.	Black core. Circular 1·8 cms. diam. Brighter in colour than previous cores. White ring 0·4 to 0·5 cms.
*E*5	0–900°C. in 12 hours. At 900°C. for 2 hours and cooling.	*No black core.* Whitish area 4 × 3 cms. *Note.* Cores still darker than those of *Da* or *Da'*.
*E*6 *E*7 *E*8	0–900°C. in 12 hours and holding at 900°C. for 2, 3 and 4 hours respectively.	No black core. White area approx. 3 × 2·8 to 3 × 2·6 cms., in these cases. No marked difference in these areas in this heating.
*E*9 *E*10	(*a*) 0–600°C. in 8 hours. At 600°C. for 6 hours, then up to 900°C. in 4 hours.	Sample, salmon pink throughout. No definite white area, showing that reducing action of carbon is probable cause of yellow areas in previous experiments.

Stated briefly, these are as follows for the Stourbridge briquettes of the size 3″ × 2·2″ × 2″, heated in a small gas-fired, muffle furnace.

1. Decomposition of the carbonaceous matter as judged by the slight change in the shade of dark grey, commences in the neighbourhood of 500°C. Oxidation, judged by the appearance of the salmon-pink colour characteristic of small amounts of ferric iron, commences at 550-580°C.

2. Oxidation of the carbonaceous matter increases as the time taken to reach a given temperature is increased and with the time of holding at that particular temperature between the approximate limits 600-900°C.

3. With a rate of increase in temperature of 75°C. per hour up to 550°C., the approximate times required to burn out

the carbonaceous matter under the conditions cited above are :—

(*a*) From 550-600°C., 0·75 hours and at 600°C. a period of 8 hours.
(*b*) From 550-750°C. 2·7 hours and at 750°C. 3 to 4 hours.
(*c*) From 550° to 900°C. 4·7 hours and at 900°C. 2 hours.

In the connection, however, the heat work which is performed on the pieces by reason of the higher temperatures in (*b*) and (*c*) must not be overlooked, as this all contributes to the elimination of carbonaceous matter.

At temperatures above 600°C. and to the limit investigated in this work, viz., 900°C., the oxidation of carbonaceous matter *is followed by the formation of a bluish white ring* which develops into a yellowish core occupying the former position of the black core in the interior of the test-piece.

This does not take place when care is taken to prevent the temperature rising above 600°C. before all the carbonaceous matter is eliminated, even on subsequent heating at 900°C. The test piece, then, shows a characteristic salmon pink colour throughout. The change, giving a yellowish interior, appears to be the result of the reducing action of the carbon on the iron compounds present. The effect, which may be only tinctorial, has also been noted in some of the samples drawn from a kiln at various intervals during burning. These yellow cores, however, may have but little practical bearing on the quality of the completely burned bricks, but definite evidence on this point has not been obtained. In fact, the opinion has been stated by several writers that even black coring developed to a mild extent in finished product has no markedly deleterious effect. It would be well-nigh impossible to prevent the formation of this yellow core under industrial conditions by reason of :—

(1) the impracticability of maintaining a strict temperature control at 600°C. and
(2) the excessive time which, as some tests not reported here indicate, would be needed to eliminate the carbonaceous matter from a full sized brick at this temperature.

Tests with a Larger Sized Piece.

At the commencement of this work it was realised that the tests on such small pieces, viz., one eighth of a full-sized brick, could at the best, give but a restricted idea of the time required for oxidation of the carbon in the bricks themselves. No suitable furnace was available for the heating of a full sized brick in the way which has been described above, but it has been possible to carry out some runs on pieces the size of a half brick. In this last case, it was found that for the Stourbridge material the heat treatment required to remove the carbon was approximately as follows :—

0-650°C. in $8\frac{2}{3}$ hours and soaking at 650°C. for a period of 24 hours.

A slight suction was used in determining this time, but the results cited below seem to indicate that this has but little effect. The carbonaceous matter was completely burnt out leaving a yellow core, 6×10 cms. in cross section.

By a comparison with the results summarised on the previous page, it will be noticed that the time required for the elimination of carbonaceous matter varies to much the same extent as does the size of the piece. Thus, for a test piece one eighth the size of a full-sized brick the time required at 600°C. is 9 hours, whilst for a piece four times as large, the time required at 650°C. is approximately 24 hours. It is interesting, here, to note that in the industrial firing of this material (in the continuous kiln), the time required to eliminate the carbonaceous matter (*i.e.*, from the commencement of oxidation to the final disappearance of the core) is approximately 32 hours. This result agrees very well with the one reported for the half-brick.

Effect of Draught or of Suction.

Some experiments were made in order to examine the effect of a draught or of suction on the oxidation. In a few cases, the air was removed from the surface of the test piece by suction, provision being made for its replacement by fresh air, by means of holes in the front of the furnace. This arrangement was then changed to one in which a gentle blast of air was actually blown into the interior of the muffle. In neither case, however, did these modifications appear to alter the extent of the oxidation produced in a given time, and it was concluded that the original conditions were such as to exclude any hampering of superficial oxidation, at least, by a badly ventilated atmosphere, or by the formation of a "buffer" of steam surrounding the piece. At the most, given a well-ventilated and oxidising atmosphere surrounding the piece, a draught would be expected to have but little effect on the interior of the piece itself. In the interior, a very complex state of affairs most likely exists. There are present probably free carbon, carbon monoxide and dioxide together with compounds of iron all trying to attain some sort of equilibrium in the presence of the varied constituents supplied by the clay itself. The diffusion of the necessary oxygen and ultimate removal of the oxides of carbon formed in a structure such as the interior of a brick affords, must, it seems, necessarily be a slow and difficult process.

Tests with a Yorkshire Fireclay.

A different type of clay, one from Yorkshire, was next investigated. The results (half-brick samples were used), are presented in Table V.

TABLE V.

A Yorkshire Fireclay.

Laboratory Mark	Heat Treatment	Remarks
*F*1	0–650°C. in $8\frac{2}{3}$ hours. At 650°C. for $5\frac{1}{3}$ hours. Cooling in furnace. Suction = 15 ins. H_2O.	Black core 8·7 × (5·5-6) cms. Faint bluish with ring round the core. Remainder cream coloured.
*F*2	(*a*) 650°C. in $8\frac{2}{3}$ hours. At 650°C. for $5\frac{1}{3}$ hrs. coolong in muffle. (*b*) *Oo*–650°C. in $2\frac{1}{2}$ hours At 650°C. for $11\frac{1}{2}$ hrs. Cooling in muffle. Toral time at 650°C. = 17 hours approx. Suction = $15\frac{1}{2}$ ins. H_2O	Black core 6·4 × 2·1 cms. No white ring only a shading off from black of core to cream colour of remainder of the piece.
*F*3	(*a*) and (*b*) as in *F*2. (*c*) 0–650°C. in 2 hours. At 650°C. for $3\frac{2}{3}$ hrs. Cooling in muffle. Toral time at 650°C. = $20\frac{1}{2}$ hours. Another 2 hours at 650°C. probably necessary to burn out *C*. Suction = 15-16 ins. H_2O.	Black core 1·5 × 3 cms. only a shading off as in *F*2. Remainder cream coloured.

The last run, *F*3, shows that a period of $20\frac{1}{2}$ hours at 650°C. does not quite eliminate the carbon. A slight black core remains, but a further soaking for 2 hours would most probably remove it. Comparing this result with the Stourbridge, it will be seen that there is no great difference between the two in the matter of the times required, which lie far nearer to each other than would be expected from two such different materials.

There is a further point to be noticed and this is in connection with the development of yellow cores. In this last clay there is no such development and this is in accord with the fact that the material from Yorkshire contains a lower iron content, judged both by the cream colour developed on burning and by the results of the analysis given.

This further supports the idea previously advanced that it is the iron present together with carbon which produces this yellow area or core so prominent in the Stourbridge material.

Tests with a Scottish Fireclay.

The Scottish firebricks did not show any pronounced develop-

ment of black cores and the elimination of carbon could not be followed in the distinct way which was possible with the other two clays studied. Few tests were, therefore, carried out on this material from the point of view of the elimination of the carbon. When heated from 0-600°C. in 4 hours the pieces (3″×2·4″×2″) showed a dull, black interior surrounded by a white exterior. With a heat treatment of 0-600°C. in 8 hours this suggestion of a core had disappeared. Further experiments on the firing of the Scottish material have shown that the carbonaceous matter is completely removed when the time taken to raise the temperature of the kiln (containing 600 bricks) from 500°C. to 1100°C. is not more than 20 hours.

The Data of Specific Gravity, Porosity and "Loss on Ignition."

These determinations were made particularly to correlate certain changes with time and temperature. Further, they have been used to check the results obtained in the work on the changes taking place during industrial burning, since the temperature measurements in this latter work were open to doubt, and the effect of the kiln atmospheres hardly understood.

TABLE VI.

Showing certain data concerning the Test Pieces of Stourbridge Product.

Mark	Heat Treatment.	True Specific Gravity		True % Porosity. (Av. val.)	% Loss on Ignition	
		Exterior	Interior		Exterior	Interior
*D*7	0–400°C. in 6 hours.	2·610	2·596	25·5	11·10	11·42
*D*9	0–500°C. in 8 hours.	2·597	2·597	27·5	7·46	10·30
*D*4	0–600°C. in 4 hours.	2·594	2·607	28·5	7·18	9·72
*D*1	0–600°C. in 8 hours.	2·585	2·576	29·8	6·36	9·12
*D*5	0–600°C. in 12 hrs.	2·553	2·539	30·8	2·80	5·72
Do	0–620°C. in 8 hours. Cooling in muffle. 0–600°C. in 2 hours and holding at 600°C.	2·556	2·559	33·2		
Dp	for 11 hours.				1·60	1·66
De	0–750°C. in 10 hrs.	2·564	2·552			
Dj	0–750°C. in 10 hrs. Cooling in muffle. 0–750 in 2½ hours and holding at 750°C. for 7 hrs. Cooling in muffle.	2·586	2·581	33·3		

Mark	Heat Treatment	True Specific Gravity		True Percentage Porosity. (Average value).
		Exterior	Interior	
Dm	0–750°C. in 10 hours and holding at 750°C. for 1½ hours. (cooling in muffle). 0–750°C. in 2½ hours and holding at 750°C. for 11½ hours. Cooling in muffle. Total hours at 750°C. = 13.	2·587	2·584	33·6
*E*1	0–900°C. in 12 hours.	2·591	2·601	33·5
*E*8	0–600°C. in 8 hours. 0–600°C. in 2 hours then holding at 600°C. for 6 hours, up to 900°C. in 4 hours.	2·635	2·636	32·7

It can readily be seen that the decrease to a minimum in true specific gravity occurs in the neighbourhood of 600°. This is very likely connected with the dehydration of kaolinite. From these results, also, the effect of time in completing such a change is indicated, for, with *Do*, it seems that the whole of the kaolinite has been dehydrated, since both the interior and exterior values show an increase. Practically complete dehydration is also indicated by the "loss on ignition" result for *Do*. The rise in specific gravity from 600° to 900, which has been noted in the aforementioned work, is well shown. In this connection a comparison of *E*1 and *E*9 is interesting. It seems that the removal of the carbonaceous matter previous to raising the temperature to 900°, has a decided effect on the specific gravity.

It is generally supposed that maximum porosity occurs in the neighbourhood of 750°. The results for *Do*, *i.e.*, continued heating at 600°, show that, to all intents and purposes, maximum porosity can be obtained at 600°C.

The "loss on ignition" data indicate roughly the effect of time on the breakdown of kaolinite, and help to expand the conclusions drawn from the specific gravity values.

In conclusion, the authors wish to thank Mr. H. Edwards, of the Testing Department of the Central School of Science and Technology, for continued help during the progress of the work.

XVI.—The Relation between Under-Load Refractoriness, Ordinary Refractoriness, and Composition, Physical and Chemical, of Refractory Materials. Part II. (Firebricks—*continued*.)

By A. J. Dale, B.Sc., A.I.C.

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In an introductory report, Pt. I. (Trans., **23**, 217, 1924), the determinations carried out in connection with this work have already been outlined, together with the methods and apparatus of experiment. A number of results were therein presented showing the chemical and certain physical properties of laboratory-made firebricks and dealing in some detail with the subsidences occurring when such material was subjected to comparative heat treatments under a static load.

In order to obtain, if possible, more definite information regarding the nature and amount of the load-subsidence of firebrick material at temperatures within the softening range*, one series of determinations involved a measurement of the rate and amount of deformation occurring at 1,350°C. It was hoped that the results so obtained would afford evidence for, or against, accepting the cone at which a firebrick material completely fails under load as a criterion of the true load-bearing capacity of that material. These results, in the case of the *S* bricks, were reported in Pt. I., (Trans., **23**, 231, 1924, Fig. 11); those obtained with the remaining series of bricks are accordingly presented in this paper, together with a complete examination of bricks from another fireclay, Lab. mark *U*, and a selection of typical commercial firebrick products. The complete data put forward in this paper and in Pt. I., are discussed in some detail, and the conclusions from this work coupled with the previous reports of Mellor, Moore, Emery, Bradshaw and others[1], are summarised.

Results of Examination of a North of England Fireclay.

Following out the procedure described in Part I., four sets of bricks were made up from a high grade fireclay, Lab. mark *U*, viz., straight clay and grogged bricks with 20, 40, and 60% grog respectively.

U Clay, Chemical Analysis.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	Loss
46·52	1·79	34·79	2·26	0·13	0·04	0·56	0·28	13·70

*For the purposes of this paper the term "Softening Range" is intended to imply that range of temperature limited by the temperature at which subsidence under a load of 50lbs. per sq. in. just becomes appreciable, and the temperature at which complete failure occurs.

Calculated Rational Analysis.

Clay	Felspar	Quartz	Iron oxide	Lime
85·74	4·96	3·47	2·26	0·40

Grain Size Analysis and Surface Factor.

On 100s Lawn.	On 200s.	In Elutriator.	Carried Over.	Surface Factor.
5·35	0·68	2·03	1·94	85·1

Refractoriness of Raw Clay. Cone 31.

Physical Data of Fired Products.

	% Vol. Contraction.		Apparent % porosity	Ord. Refract. in cones
	Wet/dry.	Dry/Fired.		
U straight clay	12·00	18·36	22·1	31
U 20% grog ..	6·07	14·19	27·3	31/32
U 40% grog ..	6·7	1·06	32·3	32
U 60% grog ..	very low	1·07	32·8	31/32

BEHAVIOUR UNDER LOAD (50 lb. sq. in.) OF U BRICKS UP TO POINT OF COMPLETE FAILURE. (SERIES I.)

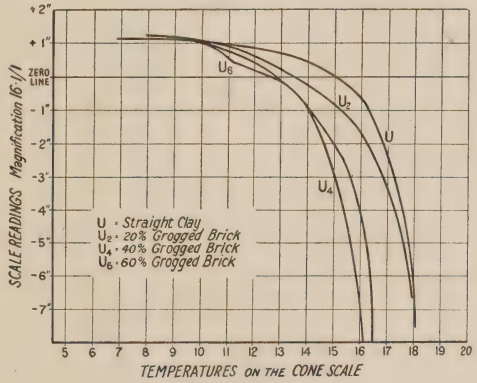

Fig. 1.

The subsidence—temperature relations of the *U* straight clay and grogged bricks are recorded in Fig. 1. It will be noted that the general nature of these curves is comparable with those reported in Pt. I., Figs. 3 to 7 (TRANS., **23**, 226, 1924). The 60 per cent. grogged brick, however, appears to fail completely at a slightly higher temperature than the 40 per cent. grogged brick.

BEHAVIOUR OF THE *M*, *C*, *B*, *A* AND *U* BRICKS UNDER LOAD AT 1,350°C. (SERIES II.)

The method of carrying out this determination has already been described (Pt. I.) and the remaining curves of series II are presented in Figs. 2, 3, 4, 5, 6. The determination involves heating up the test piece under a load of 50lb. per sq. inch at a constant rate of

rise of temp. of 50° per five minutes until 1,350°C. is attained. The temp. is then maintained constant for two hours, during which period the subsidences are recorded. The general nature of these curves will be recognised together with the almost general effect of increasing grog content (and to a certain extent, increasing porosity). The accuracy of the series II. determinations is undoubtedly of a higher order than that attainable in Series I.; and, furthermore, since it is probable that the phenomena concerned are simpler than in the Series I. determinations, it is preferable to consider first in some detail these subsidences at a constant temperature.

(NOTE:—In Figs. 2, 4, 6, 13, 14, 15 and 16, the curves are separated in order to bring out the salient points. The correct positions of the individual curves are indicated on the graphs.)

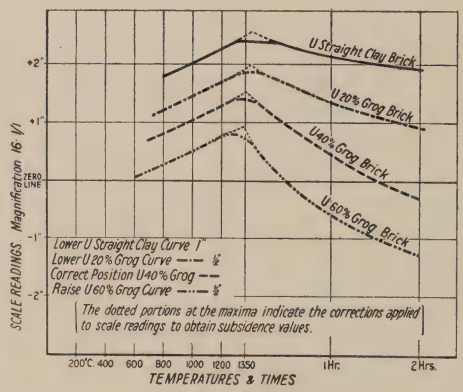

Fig. 2.

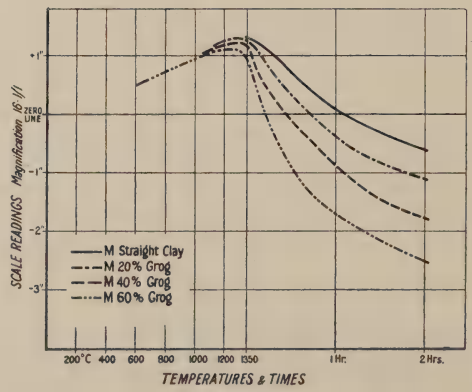

Fig. 3.

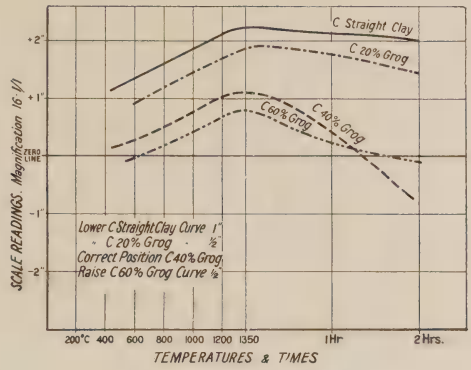

Fig. 4.

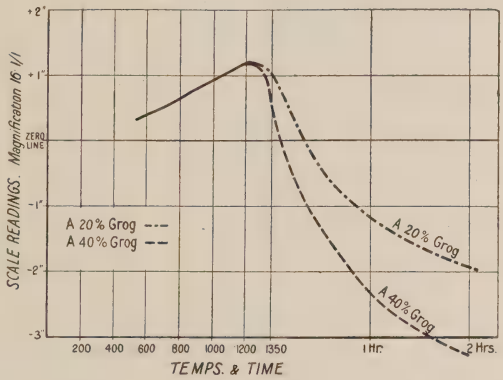

Fig. 5.

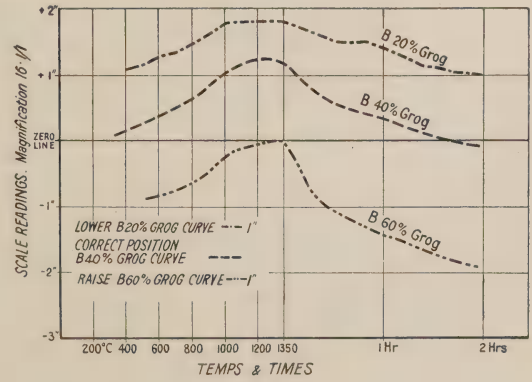

Fig. 6.

A. Detailed Considerations of the Curves of Series II.

1. In each case, the first or ascending portion of the curves represents the thermal expansion under a load of 50 lb. per sq. in. of the test piece, the thrust rod and the basal supports and furnace bed. Since preliminary determinations have shown that the carborundum thrust-rod and supports display an almost linear thermal expansion under load up to temperatures higher than 1,350°C., it follows that any marked fall from the linear of the ascending portion of the Series II. curves marks, at least, a diminution in the coefficient of thermal expansion of the test piece under load. (For corresponding temperatures see Table I.)

2. The second and comparatively flat portion of the curves records the mean of the two simultaneous occurrences, the thermal expansion of the thrust rod, supports, etc., and a gradual subsidence of the test piece. At some temperature between the commencement of the flat portion and the point at which initial lagging of the ascending portion occurs, the brick under test is unable, during this *initial* heating after kiln firing, to support a load of 50 lb. per sq. in. without subsidence. This temperature interval appears to be a critical range of some importance and the values in the case of the experimental bricks examined are set down in Table I.

Apart from the limits indicated in Table I., it is interesting to note that the 40 per cent. grog bricks of the *S*, *B* and *C* series show a diminution of the coefficient of thermal expansion under load at temperatures lower than with the other bricks of the same series.

3. When the required temperature of 1,350°C. is reached, the dimensions of the thrust rod, etc., remain practically constant, apart from a small thermal expansion following thermal conduction, so that the third (descending) portion of the curve records the rate at which load-subsidence proceeds, the centigrade temperature on the exterior of the brick remaining constant. The temperature on the cone scale is *not* constant during this heat soaking period. As 1,350°C. is reached, cones 7 or 8 are usually down, followed quickly by cones 9 and 10, while after a further two hours, cone 13 is down and cone 14 well over. The cones, therefore, afford a good check on the actual heat treatment to which the brick is subjected.

B. An Empirical Relation between Subsidence and Time. (Load and Cent. Temp. Constant).

The comparatively simple form of these series II. curves suggested that the behaviour of a firebrick under conditions applying during this test, may be defined by an empirical relation of the form

$$d = kt^m$$

where d=deformation or vertical subsidence indicated by the recording pointer; t=time of heat soaking at 1,350°C. at which a subsidence d had occurred, and k and m are constants character-

TABLE I.

Showing "Critical Range," limited by Centigrade Temps. at which (*a*) Coeff. of Thermal Expansion Under Load diminishes and (*b*) Subsidence becomes apparent.

	(*a*) (*b*)		(*a*) (*b*)		(*a*) (*b*)
Straight *S*	1,060° to 1,140°	Straight *C*.	1,280° to 1,350°	Straight *A*	Not Detd.
S 20% Grog	1,100° ,, 1,170°	*C* 20% Grog	1,290° ,, 1,350°	*A* 20% Grog	1,200 to 1,200°
S 40% ,,	1,020° ,, 1,100°	*C* 40% ,,	1,200° ,, 1,350°	*A* 40% ,,	1,200 ,, 1,200°
S 60% ,,	1,100° ,, 1,180°	*C* 60% ,,	1,280° ,, 1,350°	*A* 60% ,,	Not Detd.
Straight *B*	Not Detd.	Straight *M*	1,200° to 1,280°	Straight *U*	1,220° to 1,350°
B 20% Grog	1,000° ,, 1,200°	*M* 20% Grog	1,200° ,, 1,260°	*U* 20% Grog	1,240° ,, 1,320°
B 40% ,,	900° ,, 1,200°	*M* 40% ,,	1,180° ,, 1,250°	*U* 40% ,,	1,280° ,, 1,320°
B 60% ,,	1,000° ,, 1,320°	*M* 60% ,,	1,140° ,, 1,240°	*U* 60% ,,	1,220° ,, 1,260°

Determinations on the straight *A* and *B* bricks were not carried out owing to the cracked nature of the fired products. A 60% grog was far too friable, and obviously unsuited for practical purposes.

istic of the material under test. If a relation of this type is applicable, log.d plotted against log.t should give a straight line. On trial it was found that the data obtained with the S, M, A and U straight clay and grogged bricks satisfy this condition (see Figs. 7 and 8.) Owing to the uncertainty of the actual value of d with

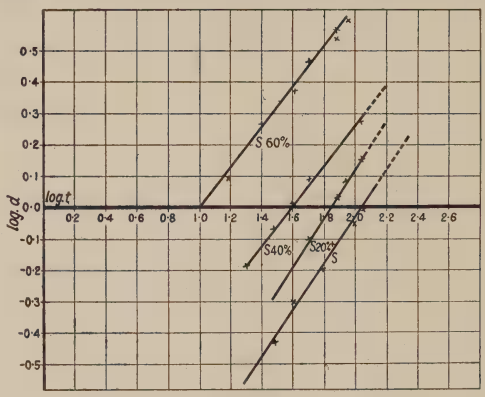

Fig. 7.

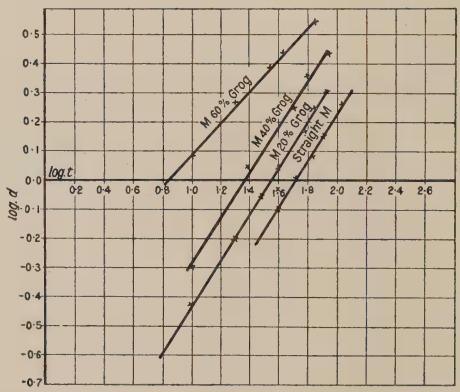

Fig. 8.

the B bricks which had obviously (see Fig. 6) undergone an appreciable amount of subsidence before 1,350°C. was reached, it was not expected that the data would be applicable to this relation. With the C series, the data of the 20 per cent. grog brick conform with an equation of the above type, but the data with the other C bricks appear to constitute exceptions. The excellent agreement, however, (see Figs. 7 and 8 and Table II.) obtained with the straight clay and grogged bricks of the four distinct series S, M, A and U justifies a more detailed consideration of this empirical relation.

C. The Value and Significance of the Constants.

It can be shown that the constant k in the above equation $=\left(\frac{1}{a}\right)^m$, where a=time required for the first arbitary unit subsidence (indicated by the scale reading)=antilog. of the intercept of the log. line on the log.t axis. Fig. 7 and 8, *i.e.*, re-writing the relation $d=kt^m$ in a slightly modified form,

$$d=\left(\frac{t}{a}\right)^{m}.$$

where, assigning definite values to the units, a=time in mins. required for the first inch subsidence deflection of the indicating pointer attached to the test furnace, m=tangent of the angle the log. curve makes with the log.t axis, (see Fig. 7). The values of the constants m and a can be read off from the graphs or calculated from the available data. The results in the case of the *S. M. U.* and *A* bricks are arranged in Table II. They may be regarded as summing up numerically the characteristics of the third portion of the Series II. curves and may possibly constitute a measure of the refractory value of a brick under load conditions. The percentage "after-contractions under load" of the bricks are also shown. This quantity indicates the percentage diminution in the *length* of the piece as shown by cold measurements taken before and after the test. This squatting in a vertical direction is accompanied by an indefinite lateral bulging.

TABLE II.

SHOWING a AND m AND % SUBSIDENCE DURING THE 1350°C. TEST.

	(m)	(a)	% Subsidence
Straight *U*	0·85	462	0·91
U 20% Grog	0·85	110	2·06
U 40% ,, ...	0·85	60	3·02
U 60% ,, ...	0·69	34	3·85
Straight *S*	0·74	115	1·60
S 20% Grog	0·77	72	2·19
S 40% ,, ...	0·67	40	2·65
S 60% ,, ...	0·64	10	5·16
A 20% Grog	0·52	13	5·84
A 40% ,, ...	0·52	5	8·75
Straight *M*	0·81	53	2·30
M 20% Grog	0·79	35	4·54
M 40% ,, ...	0·78	23	5·92
M 60% ,, ...	0·54	7	5·23
Straight *C*	—	—	0·62
C 20% Grog	1·60	219	1·01
C 40% ,, ...	—	—	2·22
C 60% ,, ...	—	—	1·70
Straight *B*	—	—	—
B 20% Grog	—	—	0·99
B 40% ,, ...	—	—	2·15
B 60% ,, ...	—	—	3·35

Examination of the figures in Table II. shows that for a specific clay and graded grog similar in composition, increasing the grog content causes a marked diminution in the numerical value of a. The value of m in the U, M and A Series is not materially altered by increasing the grog content up to 40%. The change from 40% grog content to 60% grog content, however, results in a marked diminution of the constant m. With the S series, a similar diminution in the value of m is noticeable with increased grogging. The fact that m possesses a lower value with the highly grogged bricks than with the straight clay products may be a point of considerable importance, as the following reasoning will show. A casual examination of the Series II. curves for any of the bricks might lead us to prefer a straight clay brick to a grogged brick when resistance to deformation was a primary consideration. For example, the fact that the straight M brick (Table II. and Fig. 3) exhibits only a 2·30% subsidence whilst the M 60% grog brick deforms to the extent of 5·23% (at 1,350° for 2 hours) certainly appears to indicate the better value of the straight M brick from the load bearing point of view.

The Standard American Load Test[2] involves this assumption. A more detailed consideration of the problem, however, indicates how fallacious such an assumption may prove to be in certain cases.

Consider the equation $d = \left(\frac{t}{a}\right)^{m}$.

The second differential of d with respect to t,

$$i.e., \quad \frac{\delta^2 d}{\delta t^2} = m.(m-1)\ a^{-m}.t^{m-2}$$

Now the second differential coefficient is a measure of the acceleration* with which deformation occurs, and it follows from the above that the greater the value of m for a given value of a, the greater the acceleration of the subsidence. The fact that with the straight clays a has a greater value than with the highly grogged bricks, *e.g.*, M, U and S, Table II. indicates that it is merely a matter of time before the subsidence with the straight clay bricks becomes equal to the subsidence with, say, the 60% grogged brick. After a certain time, the subsidence will be equal. Beyond this time, the subsidence with the straight clay brick will proceed at a rate greater than that with the grogged brick.

Fig. 9 illustrates the point in question and the case of the M straight clay and 60% grog bricks are considered in detail below.

Consider the continuous lines in Fig. 9 as representing the behaviour of the M clay and 60% grogged bricks during the first two hours load treatment at 1,350° (Series II. determinations). Following out the above reasoning, it becomes apparent that, after a certain time has elapsed, the deformations, d, will become equal

* With the proper sign prefixed.

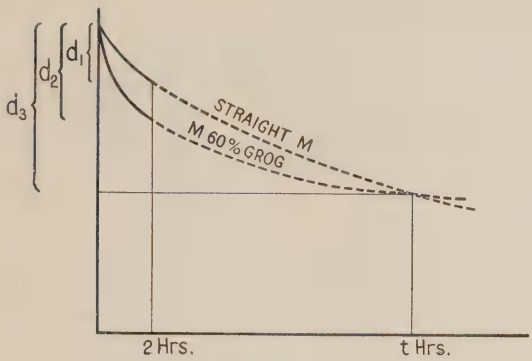

Fig. 9.

in amount, and beyond this time the deformation with straight clay brick will proceed at a greater rate than with the 60% grogged brick. Considering the definite example of the *M* straight clay and the *M* 60% grogged brick, the deformations, *d*, will be equal, when a certain time, *t*, has elapsed.

Now, for the *M* straight clay brick, $a=53$ and $m=0{\cdot}81$.

$$i.e.,\ d=\left(\frac{t}{53}\right)^{0.81}$$

For the *M* 60% grog brick, $a = 7$ and $m = 0{\cdot}54$.

$$i.e.,\ d=\left(\frac{t}{7}\right)^{0.54}$$

The deformations, *d*, will be equal when a certain time, *t*, has elapsed.

$$i.e.\ \left(\frac{t}{53}\right)^{0.81}=\left(\frac{t}{7}\right)^{0.54}$$

whence $t=3{,}035$ minutes.

In other words, had the Series II. determinations extended over a period of approx. $2\frac{1}{8}$ days instead of 2 hours, the subsidence with the *M* straight clay brick would have been equal to that of the 60% grog brick; and for times in excess of that, the deformation with the straight clay brick would proceed with the greater velocity; similar reasoning applies to the *S* and *U* bricks. It is realised that with a load of 50 lb. per sq. in. rupture would probably occur before the time *t* had elapsed. The example quoted is an extreme one, but there is reason to assume that the above relation between deformation and time will hold for lower values in the loading, when *a* will probably have a greater value and the time necessary for the above state of affairs to occur will be more prolonged. It is interesting to note that, with the elastic viscous deformation of pitchy materials, Nutting[3] has shown the parabolic type of

relation to hold for variable values of the loading, the value of m being independent of the load.

Before passing on to the results obtained with a selection of commercial firebrick products, it is inferred from the above differential equation of the second order, that, should m have a value greater than unity, the deformation will proceed with acceleration instead of retardation. This point will be considered later in the paper.

Examination, Load Behaviour, etc., of a Typical Selection of Commercial Firebrick Products.

An application made to a number of manufacturers for samples of firebrick material, free from silica grog, met with a ready response and a representative selection of bricks was obtained. In many cases, manufacturers were kind enough to supply analyses and other informative data and a considerable amount of time has thus been saved. Each brick has been subjected to the following determinations:—

(*a*) Behaviour under load (50 lb. per sq. in) up to the cone at which complete failure occurs.

(*b*) Behaviour under load at 1,350° for two hours.

(*c*) Ordinary refractoriness.

(*d*) Apparent porosity.

(*e*) Examination of textures before testing and after complete failure under load has occurred.

Table III.

Showing Ultimate Chemical Analysis of Commercial Products.

	1	2	3	4	5	6	7	8
SiO_2 ..	71·38	75·00	75·50	65·80	57·57	56·38	60·00	55·90
TiO_2 ..	1·07	1·10	1·20	1·43	1·47	2·26	1·67	1·85
Al_2O_3 ..	22·27	21·00	19·50	24·12	37·54	34·46	32·46	37·58
FeO_3 ..	1·28	1·90	2·30	5·13	2·77	3·71	3·44	2·34
CaO ..	0·29	0·20	0·20	0·88	0·27	1·09	0·23	0·47
MgO ..	0·97	0·10	0·10	0·86	0·24	0·81	0·48	0·50
K_2O ..	1·81	0·60	0·70	1·16	0·31	0·70	0·80	0·56
Na_2O ..	0·86	0·50	0·50	0·30	0·17	0·36	0·42	0·38
Loss	—	—	—	—	—	—	0·20	0·06

	9	10	11	12	13	14	15	16
SiO_2 ..	55·06	55·88	75·47	74·66	70·70	59·17	53·77	24·39
TiO_2 ..	1·25	1·56	1·59	2·67	n.d.	1·40	1·95	2·16
Al_2O_3 ..	37·87	38·54	19·94	20·08	25·80	33·83	37·92	71·61
Fe_2O_3 ..	3·75	1·88	1·19	1·51	2·36	3·52	3·19	0·81
CaO ..	0·66	0·46	0·15	0·07	0·31	0·36	0·78	0·0
MgO ..	0·11	0·24	0·61	0·03	trace	0·60	0·61	0·66
K_2O ..	0·76	0·68	0·45	0·90	0·89	1·62	1·40	0·22
Na_2O ..	0·46	0·46	0·13	0·40				0·02
Loss ..	0·18	0·20	—	0·17	—	—	—	—

Textures, etc., of Commercial Products.

No. 1. Extremely dense, wire-cut firebrick, close and uniformly textured. Fairly heavily grogged, but no grog particles are greater than $\frac{1}{10}''$ diam. Complete failure under load was accompanied by approximately uniform bulging of the four faces with no defined cleavage planes or realignment of pore spaces. (*See later*). Stated by makers to be in demand for lining steel-ladles.

No. 2. Machine-made firebrick; close textured, very few grog particles larger than $\frac{1}{10}''$; grog particles subangular to rounded; sparsely distributed iron specking. After complete failure, piece showed marked bulging of the four faces with badly defined trace of an incipient diagonal cleavage plane, which apparently would have been more marked had the subsidence been allowed to proceed further.

No. 3. Hand-made firebrick, product of same firm as No. 2. Texture comparable with that of No. 2. Failed under load with marked bulging of sides of piece and signs of incipient diagonal fracture; angle of inclination 40° to 45° to horizontal. Realignment of larger pore spaces (see Fig. 10).

No. 4. Machine-made brick; numerous small black specks of apparently unoxidized shale; abundance of subangular, grog particles, none exceeding $\frac{1}{10}''$ diam; fairly open texture. After failure, the piece showed bulging of all four faces without appearance of any cleavage plane.

No. 5. Hand-made firebrick. Fairly close textured with tendency toward laminations. Graded, angular to subangular particles, many showing dark cores; largest grog approx. $\frac{1}{8}''$ diameter; sparse iron-specking in the matrix. After failure under load, piece showed little bending of the faces,

but a marked diagonal cleavage plane inclined at 45° to 60° to the horizontal. No obvious rearrangement of the pore spaces.

No. 6. Close and uniformly textured firebrick; graded angular to subangular grog, many of the grog particles being dark-cored. Largest grog $\frac{1}{8}''$ diam. Numerous iron specks, small and large, throughout the brick.
Failure under load accompanied by double diagonal V break, apex upwards, with angles of inclination approx. 60° to horizontal. (See Fig. 17).
Bending restricted mainly to the pair of opposite faces not traversed by the fracture. No obvious tendency towards realignment of visible pore spaces.

No. 7. Uniformly textured firebrick. Abundant angular to subangular grog, largest particles $\frac{1}{6}''$ diam. Numerous small iron specks. Failed under load with bending of faces confined to one pair of opposite sides (*cf.* No. 6). Incipient diagonal fracture, angle of inclination 40° to 45° to horizontal. Slight tendency towards realignment of pore spaces.

No. 8. Remarkably close-textured exterior extending inwards to a depth of $\frac{1}{2}''$. Very open textured interior, but no dark coring. Negligible iron specking. Largest grog, approx. $\frac{1}{6}''$ diam.
Failed under load with bulging of all four faces but no defined cleavage planes.

No. 9. Close-textured, semi-vitrified firebrick; heavily grogged, grog particles subangular to rounded, largest approx. $\frac{1}{8}''$ diam. Abundant iron specking. Failed under load with fairly equal bulging of all exposed faces; ill-defined tendency towards a diagonal fracture; no marked realignment of larger pore spaces.

No. 10. Close and uniformly textured firebrick; angular to subangular with few particles larger than $\frac{1}{10}$; comparative absence of iron specking. Limited friability when outer surface has been removed. Failed under load with little bending of faces apart from actual dislocation following breakdown of the brick along two well defined planes arranged V shape, apex upwards; angles of inclination approx. 70° to horizontal. No appreciable tendency towards pore realignment.

No. 11. Open-textured firebrick. Subangular to rounded grog, largest particles $\frac{1}{4}''$ diam. Localised iron specking, numerous pinhole pores in matrix. Failed under load with marked bending of one pair of opposite faces, (*cf.* No. 6), accompanied by a diagonal cleavage plane, angle of inclination approx. 50° to horizontal. Distinct tendency towards realignment of larger pores (see Fig. 10).

No. 12. Close-textured firebrick; numerous pinhole pores; graded grog, all particles apparently less than $\frac{1}{10}$ diam. Abundant iron specking. Fails under load with fairly uniform bulging of the four faces.

No. 13. Coarse-textured, heavily grogged retort material, friable; rounded grog particles, largest greater than $\frac{1}{3}''$ diam. Fails under load with bulging of all four faces; no defined cleavage plane but a realignment of pores in middle portion of piece, into a direction making an angle of 50° to horizontal. This phenomenon was appreciable on only one pair of opposite faces.

No. 14. Close-textured firebrick, semi-vitrified, showing a certain continuity between matrix and grog; tendency towards laminations; grog angular to subangular with limited number of particles between $\frac{1}{10}''$ and $\frac{1}{8}''$. Fails with marked bulging of four faces of piece and incipient diagonal break, angle of inclination 45° to 60° to horizontal. Signs of pore realignment.

No. 15. Light coloured firebrick; close-textured, laminated structure; graded grog with particles up to $\frac{1}{10}''$ diam.; almost free from iron specking.
Fails under load with bulging of one pair of opposite faces; diagonal cleavage plane, angle of inclination 50° to horizontal. Marked realignment of larger pore spaces.

No. 16. One of a batch of experimental Indian Sillimanite bricks for which I am indebted to Mr. W. Emery. Close-textured, natural, graded sillimanite, containing corundum, bonded with $17\frac{1}{2}$ per cent. of a ball clay previously examined in this work (See B. Series, Part I., and also this paper). Fails under load with a double diagonal, inverted V. break approx. 65° to 70° to horizontal. No appreciable pore realignment.

Types of Failure of Firebrick Material under Compressive Stress at High Temperatures.

Before proceeding with any attempt at generalisation or correlation of the comparatively large amount of data at our disposal, it is considered preferable to deal in some detail with the nature of the breakdown of the pieces. The fact that apparently failure of refractory material under load at high temperatures may occur in at least two ways, according to the nature of the material (the bulged squatt and the diagonal fracture, see Figs. 17 to 20), appears to complicate an already complex set of phenomena.

The appearance of the bricks after failure, however, shows that

(*a*) Bricks which fail with a marked bulging of the faces may, nevertheless, show signs of an incipient diagonal fracture.

(*b*) Bricks which fail with a well-defined diagonal fracture show, in addition, a certain bulging of the faces, but it is significant to note that, with these bricks, failure occurs only when a comparatively small amount of subsidence has occurred.

A probable explanation of the two types of failure is given later. In connection with the diagonal fracture, V. Bodin[4] has levelled a direct criticism at the Mellor and Moore apparatus and results. Using an elaborate, modified Frémont metal-testing apparatus, Bodin obtains such high crushing strengths for fireclay products as 20, 40 or even 60 kg. per sq. cm. at 1,500°, approx. Cone 18 (*i.e.*, from 6 to 18 times the strength one might expect from the Mellor and Moore results for similar materials at similar temperatures); he proceeds to attribute the comparatively low crushing strengths suggested by the Mellor and Moore results to an unavoidable eccentricity in the loading. This, he says, results in a shearing effect which causes early fracture along an inclined plane. In this Bodin makes the serious error of attributing to a defect in the testing apparatus a result which is governed essentially by natural laws.

The fact that ductile materials under compressive stress exhibit lateral expansion is evidence of the extremely complicated system of internal stresses involved during deformation under load; and the additional fact that numerous types of constructional and other materials, *e.g.*, cast iron, timber, limestone, asphalt, bricks, concrete, etc., fracture along definite inclined planes has, for many years, been accepted by engineers as a characteristic feature of such materials, and as evidence that the nett result of the complicated system of internal stresses is summed up, so far as rupture is concerned, by two resultants acting respectively parallel and perpendicular to the plane along which rupture occurs.

The experimental work of J. J. Guest[6], followed by that of E. L. Hancock[7] and others, resulting in the "Guest Theory," related the angle of inclination of the breaking plane with the internal friction and inter-particle cohesion of the material and has led W. W. Emley[8], to suggest the determination of the inclination of the break as a measure of plasticity. Regarding the alternative test suggested by V. Bodin[4], it is important to note that the procedure adopted by him involves

(*a*) The use of a cubical test piece of side less than 1″ (20 mm.).

(*b*) The application of the load in a time interval of one minute or less when the piece has attained the required temperature.

In connection with (*a*), Prof. Perry[9] has stated that the use of cubical test pieces yields results far in excess of the true crushing strength of the material. This is substantiated by experimental evidence.[10] (*b*) Dickenson,[11] working on the tensile strengths of steels at a red heat has stated that, from a quantitative point of view, the results obtained by rapidly applied loading are so much in excess of the true resistance of the material to deformation as

to be useless; whilst recent work on the rapid loading of refractories[12] at temperatures of 1,000° and above has proved that the strength so determined is so largely a function of the rate of increase of the loading as to render the results illusory and practically meaningless.

In concluding this section, Fig. 10, which illustrates the appearance of the faces of certain of the pieces after subsidence, is not without interest. Several of the pieces after failure show this

Fig. 10.

curved laminated structure on the pair of opposite faces traversed by the line of fracture. Generally speaking, the curvature of the lines is such that they cross the fracture plane at right-angles and bend round so as to become parallel to the top and bottom faces of the piece. For this reason, the author prefers to regard the lines as resulting from a flattening and linking up of the originally irregularly orientated pore spaces. Their appearance certainly affords evidence as to the main stress distributions within the piece and may possibly have a useful application from the constructional engineering viewpoint. In this connection, it is significant to recall that Bleininger and Brown[13] have shown that failure along a diagonal plane occurred when a single test brick was replaced by a small pier of bricks.

THE SERIES I. CURVES OF THE COMMERCIAL FIREBRICKS, ETC.

The Series I. curves (Figs. 11 and 12), obtained with the bricks Nos. 1 to 16, indicate the rate at which subsidences, under a load of 50 lb. per sq. in. proceed as the temperature, indicated above 1,350° by cones placed adjacent to the test piece, is raised at an approximately uniform rate of 600° per hour. Above cone 14, this corresponds *roughly* with two cones down per five minutes. In Figs. 11*a* and 12*a*, the same data are plotted against the brick face temperatures as indicated by an optical pyrometer sighted on the carborundum adjacent to the test piece. (For more detailed information regarding the behaviour of these bricks at temperatures below cone 7, refer to the corresponding curves in Series II., Figs. 13, 14, 15 and 16). A joint consideration of the Series I and Series II. curves for any particular brick facilitates the formulation of a definite conception concerning the continuity involved in the behaviour of a firebrick under load at high temperatures from that point at which the thermal expansion falls off, to the point at which complete failure occurs.

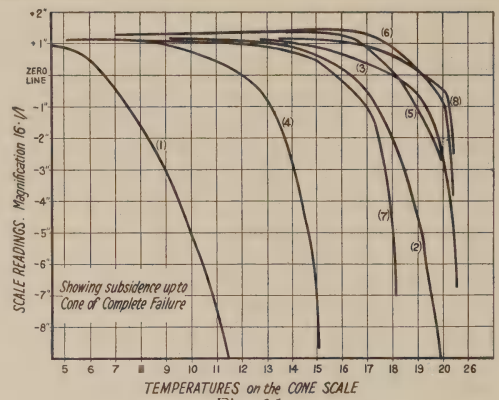

Fig. 11.

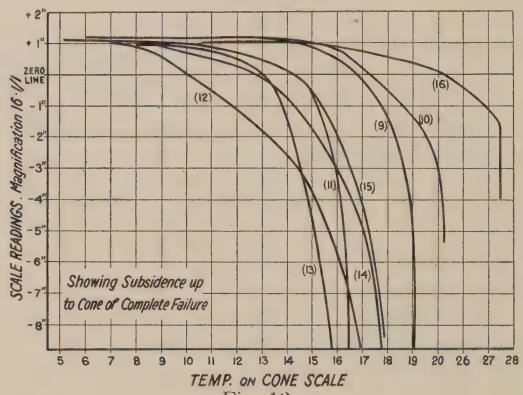

Fig. 12.

Referring to the curves in Figs. 11 and 12, (or Figs. 11*a* and 12*a*), the variable nature of the subsidence preceding complete failure becomes apparent. In some cases, *e.g.*, Nos 2, 5, 6 and 16, subsidence does not assume any marked acceleration until the temperature approaches that at which complete failure occurs, and it is significant to note that, in these cases, the diagonal type of fracture is usually well-defined. On the other hand, with certain bricks, *e.g.*, Nos. 12 and 14, the subsidence proceeds with a very gradual acceleration over a comparatively wide range of temperature. Generally speaking, however, the higher the cone at which the complete failure under load occurs, *e.g.*, Nos 2, 3, 5, 6, 8, 10, and 16, the more protracted the temperature range during which the effect of temperature on resistance to deformation is comparatively small. Conversly, marked subsidence at comparatively low temperatures, *e.g.*, Nos 1 and 4 is reflected in complete failure under load at a correspondingly low temperature.

Curves similar to these have already been reported by Endell[14]

and Steger[15] with firebricks of foreign manufacture; a collection of results obtained with such material has recently been published by Hirsch and Pulfrich[16] and shows that, with silica-alumina refractories tested under a load of 2 kg. per sq. cm. (28·5 lb. per sq. in.) the range during which appreciable subsidence occurs may be as low as 80° or as high as 500°, according to the nature of the material. The highest temperature recorded by the latter authors before complete failure occurred was 1,700°, the lowest, 1,370°. In certain cases, subsidence became appreciable at as low a temperature as 1,130°. Wilson[17] has recently published a report on the examination of a number of American firebricks by an analogous method.

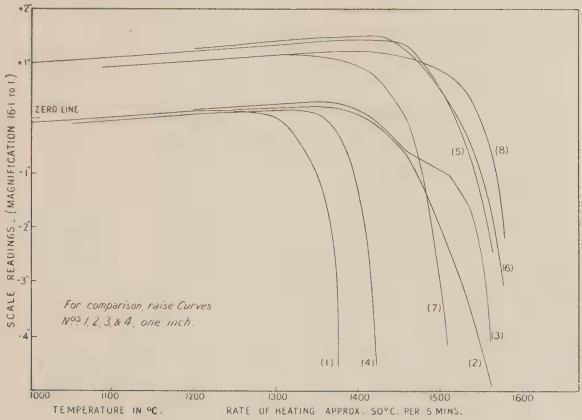

Fig. 11a.

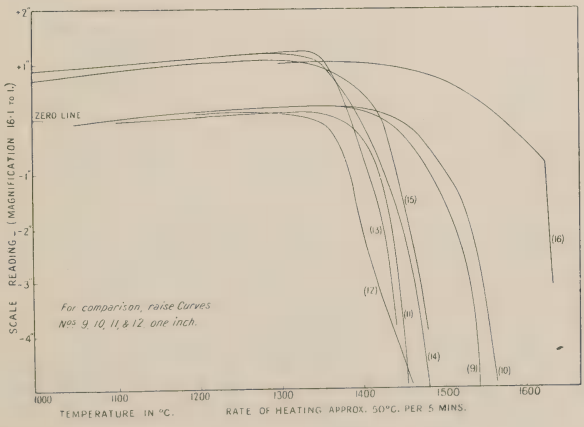

Fig. 12a.

The Series II Curves of the Commercial Firebricks, etc.

Figs. 13, 14, 15 and 16 represent graphically the behaviour of the commercial products when heated to 1,350°, at the rate of 50° per five minutes (load 50 lb. per sq. in.), the temperature being then maintained constant for a further two hours. The abscissæ therefore represent both temperature and time up to the 1,350° mark, and time beyond that point. It is interesting to note that the data relating to the descending portion of these

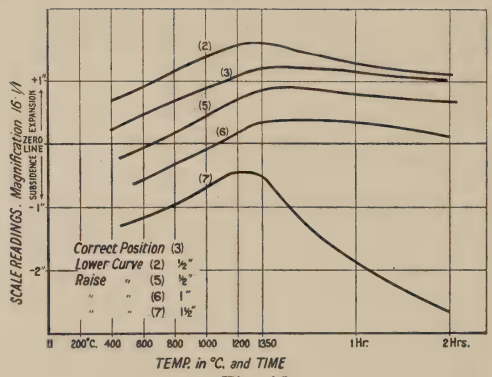

Fig. 13.

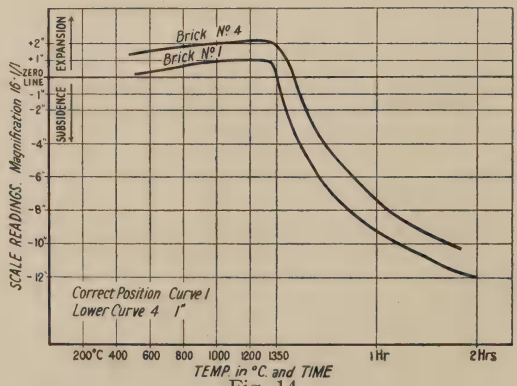

Fig. 14.

curves are connected by the empirical relation previously brought forward in connection with the experimental bricks:

$$i.e., d = kt^m. \text{ where } k = \left(\frac{1}{a}\right)^m,$$

the values of m and a being determined either by calculation or from the graphs obtained when the logs. of the subsidences are plotted against the logs. of the corresponding times. (For value of constants, see table 4.)

The second differential of d with respect to t

$$i.e., \frac{\delta^2 d}{\delta t^2} = k.m(m-1)t^{m-2}$$

is a measure of the acceleration with which the deformation proceeds. Now, when m is less than unity, the right hand side of this equation is negative; therefore, the velocity of subsidence is diminishing as time proceeds. (see Curves 12, etc., Fig. 15). When m is equal to unity the right hand side of the equation equals zero, *i.e.*, deformation proceeds with a constant velocity, (Curve No. 8, Fig. 16). When m is greater than unity the right hand side of the equation is positive, *i.e.*, the velocity of subsidence increases as time proceeds, (Curve No. 6, Fig. 13).

The significant points of the Series I. and II. curves of the commercial bricks are grouped in Table 4, together with the ap-

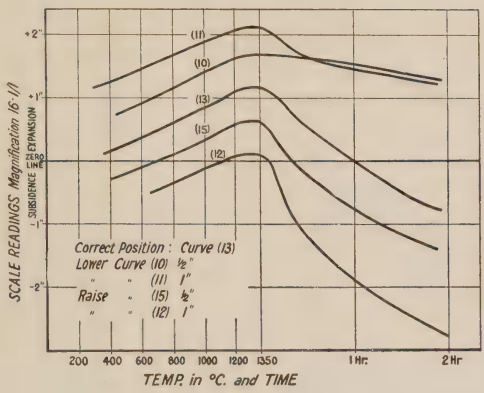

Fig. 15.

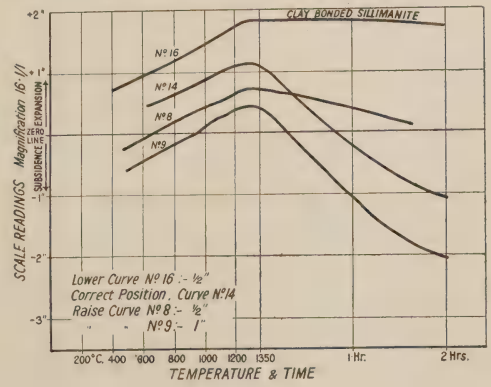

Fig. 16.

TABLE IV. PHYSICAL DATA, LOAD BEHAVIOUR, ETC. OF COMMERCIAL FIREBRICK PRODUCTS.

Brick No.	Ord. Refract. in Cones	Data from Series I. Determinations Figs. 11 to 12a.			Data from Series II. Determinations Figs. 13 to 16				% Porosity (Apparent.)
		Cone of Commencing Subsidence*	Cone of Complete Failure	Corresponding Brick Face Temperatures	Critical Range	Constants (a)	Constants (m)	% After Contraction under load	
					(1) (2)†				
1	16/17	5	11/12	1370°C.	1,000°C.– 1,260°C.	41	0·50	>20·00	12·4
2	29	13/14	20/26	1550	1,200 – 1,350	270	0·60	1·29	29·5
3	29	14/15	20	1550	1,280 –>1,350	240	1·84	0·65	25·9
4	17	9	15	1430	1,100 – 1,250	2·8	0·57	>20·00	28·1
5	32/33	16/17	20/26	1560	1,200 –>1,350	363	1·40	0·45	25·9
6	30	17/18	20/26	1570	1,300 >1,350	170	2·25	0·79	20·6
7	29	11/12	18/19	1510	1,160 – 1,280	32	0·63	3·64	22·7
8	29	16	20/26	1570	1,280 –>1,350	166	1·06	1·38	26·1
9	30	14	19	1530	1,200 – 1,320	29	0·70	4·09	21·6
10	30	15	20/26	1560	1,200 –>1,350	240	1·33	0·83	22·8
11	20	11	16/17	1460	1,200 – 1,350	118	0·58	2·28	27·1
12	30/31	8	17	1460	1,200 – 1,300	15	0·54	4·86	27·5
13	29/30	10	16	1450	1,200 – 1,340	44	0·77	3·68	24·3
14	30/31	8/9	18	1500	1,200 – 1,300	35	0·72	3·76	20·2
15	30	9	18	1500	1,200 – 1,300	32	0·70	3·35	20·7
16	>35	16	27/28	1630	1,260 >1,350	417	2·00	0·46	24·7

*When subsidence of at least 1/8 in. has occurred. †Pt. at which subsidence can be detected.
The values of the constants a and m for Bricks Nos. 3, 5, 6, 10 and 16 can only be regarded as approximate owing to the small subsidence occurring.

parent porosities. The figures included under the heading *Critical Range* indicate (*a*) the temperature at which the coefficient of thermal expansion under load first shows a lag; (*b*) the temperature at which the first definite sign of subsidence can be detected. This is a very indefinite point. It will be noted that bricks Nos. 1 and 4, possessing relatively low temperatures of failure in the Mellor and Moore test, show a lag in thermal expansion under load at the relatively low temperatures of 1,000° and 1,100° respectively (Figs. 13 and 14).

The remainder of the bricks show this lagging before 1,300° is exceeded; but 1,200° appears to be a critical temperature in the majority of cases. With Nos. 2, 3, 5, 6, 8, 10 and 16, subsidence is inappreciable at 1,350° until a certain heat-soaking has taken place. This effect may possibly be connected with the thermal conductivity of the materials.

A Suggested Classification of Firebricks based on their Behaviour Under Load at High Temperatures.

A classification of firebrick material into groups possessing characteristics which appear to be of high importance to the user of this type of material has been derived from reasoning on the following lines. A brick substance which, in the modified Mellor and Moore test, does not show marked softening at temperatures in excess of normal kiln firing temperatures, might not be expected during such kiln firing, owing to the obviously high viscosity of the matrix at those temperatures, to attain so marked a degree of interparticle, or inter matrix-grog, cohesion as a brick substance which, in the modified Mellor and Moore test, shows obvious signs of softening at relatively lower temperatures.

On the reasonable assumption[18] that resistance to deformation is mainly a joint effect of the property of internal friction (which may be summed up chiefly by the viscosity of the matrix) and the property of interparticle cohesion (including inter matrix-grog cohesion), we would expect the existence of three types of firebrick material to be demonstrated by the Mellor and Moore load test result, modified so as to include an indication of the subsidence preceding failure and also a description of the type of break. These three classes are:—

Class (*a*) With bricks of this class deformation results mainly from the effect of temperature on the property of cohesion.

Class (*b*) Deformation results principally from the effect of temperature on the viscosity of the matrix.

Class (*c*) Deformation results from a more evenly distributed effect of temperature on both the above properties.

The essentially practical signifiance of such a classification will now be demonstrated by reference to the figures in Table 4, and the load-subsidence results, Figs. 11 and 12 (or Figs. 11*a* and 12*a*) obtained with the commercial firebricks.

Class *A*.

Bricks 5, 6, 10 and 16 are excellent examples of this class. Their behaviour under load is almost incompatible with essentially viscous deformation. They failed rapidly after a gradual initial subsidence; they show little bulging of the faces except in the neighbourhood of the actual planes of fracture; portions of the piece removed from the actual fracture are undeformed (see Fig. 17), and the temperature range during which subsidence is occurring is comparatively small. Taken collectively, these facts indicate that the viscosity of the matrix is undoubtedly high, and that failure is not so much the result of diminished viscosity but rather follows a diminution in the property of cohesion and actual separation. It can be asserted, therefore, with some degree of confidence, that those firebricks, which, in this work, did not fail rapidly in the Mellor and Moore test until temperatures of cone 20 (approx. 540°C.), or above and which also conform to the limitations set out above, belong to a class of firebrick which should, owing to their comparative freedom from purely viscous deformation, satisfy the requirements for a firebrick whose predominant property is resistance to deformation at temperatures and load conditions obtaining in the carbonising industries. At the same time, it is desired to point out that such bricks, owing to freedom from softening, would preserve a hard and open texture at these temperatures; with a resulting high permeability factor which may or may not be desirable for certain purposes[19]. For example, the porosity of Brick No. 6 was only lowered by 0·9 per cent. by heating under a load of 50 lb. per sq. in. for two hours. Bricks of this class show values of m greater than unity with correspondingly high values of a (see Table 4).

Class *B*.

Bricks Nos. 1 and 4 are typical examples of this class; they show a tendency towards appreciable deformation over a wide temperature range with a comparatively low upper limit; they fail under load with a typical softening squatt (see Fig. 20), and the deformation proceeds with a gradually increasing velocity as the temperature is raised. If actual cleavage occurs, it does not assume any definite alignment. The behaviour of these bricks under load is, therefore, consistent with a continuous diminution in viscosity with rise of temperature. Brick No. 12 constitutes another example. Members of Class B examined fail under load at temperatures from cone 17 (or 1,470° to 1,480°C. on the optical pyrometer) downwards, possess relatively low values of the constants a and m as shown by their behaviours under load at 1,350° and the value of m is in all cases less than unity. (see Table 4).

Class *C*.

This appears to be an intermediate grouping into which, no doubt, the majority of firebricks will fall. It may contain bricks which are capable of sustaining a load of 50 lb. per sq. in. up to

temperatures of cone 20/26 (or greater than 1,540° to 1,550° under the test conditions) before rapid failure occurs; in other cases, members of this class may fail rapidly at cone 16/17 (or 1,460° to 1,470°). Before complete failure, these bricks show marked signs of softening accompanied by actual rupture (see Figs. 18 and 19). It appears that a true differentiation between members of this group will be arrived at from a consideration of the relative values of the constants m and a in a manner which has previously been described, but, at present, further evidence is required concerning the practical significance of the value of a, and the limiting values between which it should fall. Consideration of curves Nos. 2 and 3, (Fig. 13) indicates that bricks of this class which do not fail completely until the comparatively high temperature of cone 20 (or approximately 1,540°C.), has been attained in the Mellor and Moore procedure (Bricks 2 and 3), possess the property of high viscosity in the matrix until a comparatively high temperature, *i.e.*, higher than 1,350° has been reached. In these cases, however, when once a marked softening in the brick substance has commenced, it proceeds with a relatively rapid acceleration. It appears very possible that a proper consideration of the nature of the subsidence curve determined by the modified Mellor and Moore procedure will lead to extremely useful conclusions as to the suitability of a brick of Class *C* for a purpose where a known set of conditions exist. For example, consistent with a certain resistance to deformation, a refractory might be required which will possess a low permeability factor at working temperatures; apart from increased resistance to gas or slag penetration, this property would also suggest a marked resistance to abrasion by flue dust, etc.; and a suitably chosen refractory of Class *C* might be expected to possess, in addition to the required resistance to deformation under load, the property of developing, at working temperatures, these desirable characteristics to a degree not obtained with the non-softening members of Class *A*.

Some evidence in favour of this argument has been obtained by a re-determination of the porosities of Bricks 12 and 14, which show, after the load treatment at 1,350° a reduction of 4·7 per cent. and 3·4 per cent. respectively in the apparent porosity values.

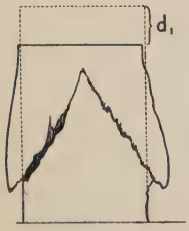

Fig. 17.

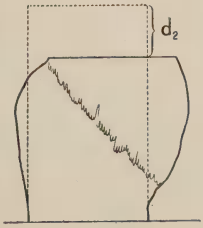

Fig. 18.

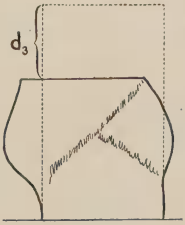

Fig. 19.

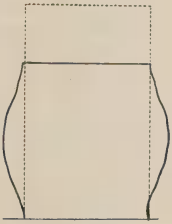

Fig. 20.

This point is brought forward as indicative of the wide applicability of the load-subsidence data representing the behaviour of the material under the modified Mellor and Moore test procedure. Figs. 17, 18, 19 and 20, reproduced from diagrams drawn to actual size in outline, from certain of the bricks after failure, demonstrate clearly the appearance of bricks of these three classes after failure has occurred.

Fig. 17, drawn from Brick No. 6, after testing, shows the comparatively small amount of subsidence, d_1, which preceeds failure with the Class *A* bricks.

Figs. 18 and 19, the outlines of bricks Nos. 15 and 2, are representative of the failures under load of Class *C* bricks.

The subsidences, d_2 and d_3 which precede rapid collapse, are greater than with Class *A*, and although there are indications of diagonal rupture planes, marked softening of the pieces has obviously occurred as is shown by the bulging of the faces.

Fig. 20 shows the softening squatt of Brick 4, typical of Class *B*. There is symmetrical bulging of the faces with no defined rupture planes. The dotted outlines in these diagrams represent the same section of the piece before testing. It is hoped that these diagrams will facilitate the visualisation of that physical distinction between the mechanism of the under load subsidences of Classes *A* and *B*, which is so apparent when the actual pieces are examined, and at the same time afford more obvious evidence of the intermediate nature of Class *C*.

Effect of Texture and Porosity on the Ordinary Refractoriness and Load Behaviour of Firebrick Materials.

The results already presented in this paper dealing with the behaviour of firebrick material at temperatures within the softening range, point to the considerable care which is necessary in any attempt at correlation of texture with the load behaviour of refractory material at high temperatures. If any connection between texture and load behaviour is to be expected, it will involve essentially the effect of the original texture on the rate of change of this texture during load treatment at elevated temperatures.

The definition of texture itself involves a consideration of:—

(*a*) The nature of the matrix, governed by the degree of vitrification, refractoriness, etc.

(*b*) The degree of cohesion between the matrix particles and the matrix and the grog, no doubt dependable on (1) the nature of the grog, angular or otherwise, chemical similarity between grog and matrix, etc.; (2) degree of kiln firing attained.

(*c*) The degree of distribution of certain undesirable minerals throughout the matrix.

It is considered desirable to make this problem the subject of a later report and to restrict the present discussion to a presenta-

tion of certain empirical facts indicated by the foregoing results.

Grog Effects.

1. With three of the experimental clay-grog Series, *B*, *M* and *U*, *B* being a readily vitrifiable ball clay yielding a smooth angular grog, *M* and *U* more highly refractory non-vitrifiable clays yielding porous grog, increasing the grog content resulted in an increase in the ordinary refractoriness. In this respect, the result with the *S* clay brick appears to be anomalous.
2. When the behaviours under load at a constant temperature of 1,350° are considered (Figs. 2, 3, 4, 5 and 6), increasing grog content almost invariably results in an increase in the rate and amount of subsidence *occurring during a limited time interval.* But it has been demonstrated previously in this paper that the rate and amount of subsidence, especially in the case of the highly grogged bricks, may, in certain cases, after a more extended time interval, be less than with the bricks of lower grog content or the straight clay bricks. The rapidity of the initial subsidence is, however, evidence of the care needed during the initial firing of a setting.
3. In so far as the experimental bricks are concerned, the cone or brick face temperature at which complete failure occurs under load of 50 lb. per sq. in. is lowered by increasing the proportion of grog with a specific clay (*cf.* Figs. 3 to 7, Pt. I., TRANS., **23, 226, 1924**, and Fig. 7 of this report).
   The generality of this statement is necessarily limited by the special conditions imposed during this work, for example, the nature of the grog grading, and the upper limit of grog content.
   That such a generalisation will not hold for other clays with a different grog grading has already been demonstrated by Mellor and Emery[20].

Porosity Effect.

The results obtained with the *S*, *B*, *C*, *M* and *A* straight clay bricks (Pt. I., TRANS., **23,** 217, 1924), and with the *U* straight clay brick (page 171), show that the relation between porosity and ordinary refractoriness is very ill-defined. The *C*, *M* and *A* clays, with which vitrification following the cone 13/14 kiln firing has obviously not proceeded to any marked extent, possess porosities and ordinary refractory values higher than those of the *B* clay brick, apparently very vitrified, and the *S* clay, semi-vitrified. When we confine our attention to the grogged bricks, there appears to be no connection between ordinary refractoriness and porosity with bricks of different ultimate chemical composition. A similar remark applies to the relation between porosity *per se* and behaviour under load. In Fig. 21, the values of the porosities of the experimental bricks are plotted against the percentage grog contents.

These curves show clearly that the rate of increase of porosity with increasing grog content diminishes as the value of the grog content increases. This fact suggests that the porosity effect in the behaviour of firebricks under load at high temperatures is intimately connected with a texture efect involving the *nature* of the porosity, as suggested by Green[19] in his consideration of thermal conductivity.

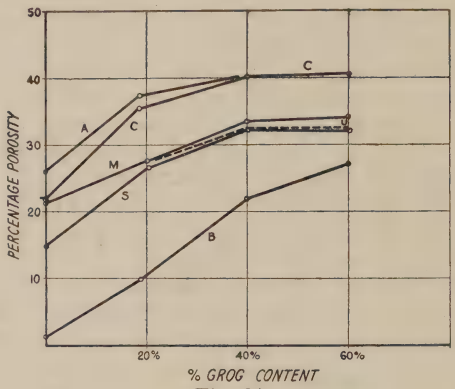

Fig. 21.

Relation between the Ordinary Refractoriness and the Behaviour Under Load of Firebrick Materials.

Of the sixteen commercial firebricks examined, the two which gave decidedly low values in the ordinary refractory test, Nos. 1 and 4, also failed at comparatively low temperatures in the Mellor and Moore test, showed evidence of marked softening at relatively low temperatures and subsided to an extent greater than 20 per cent. of their original length when treated under load at 1,350° Conversely, sillimanite brick No. 16, with an ordinary refractoriness greater than Cone 35, did not fail in the Mellor and Moore procedure until cone 27/28 (1,620° to 1,630° on the pyrometer) was attained, showed little traces of softening during subsidence and, after heating under load at 1,350° for two hours, the diminution in length was only 0·46 per cent. If, however, the china clay (*C*) experimental bricks be left out of the consideration, there is little evidence in the ordinary refractory results of the remaining 37 experimental and commercial bricks which can safely be relied upon as affording any indication of the behaviour of these products under load conditions at elevated temperatures. In some cases, the result of the ordinary refractory test is extremely misleading if we are to accept a suitably interpreted result of either of the load tests applied in this paper as indicative of the tendency of the bricks to deformation in commercial settings where stresses, due either to superincumbent weight or to restricted thermal expansion, may assume appreciable magnitudes. For example, brick No. 11 with an ordinary refractoriness

of cone 20, is more capable of resisting deformation (as exemplified by the curve obtained by either load test), than brick No. 13 or the experimental grogged bricks of the *S* series, which possess ordinary refractory values four or four and a half cones higher.

Brick No. 6, ordinary refractoriness cone 30, stands up much better under load than Brick No. 12, ordinary refractoriness cone 30/31, while at the same time the characteristics of the subsidence curves either in series I., Figs. 11, 11*a*, 12, and 12*a*, or in series II., Figs. 13 and 15, are entirely dissimilar.

Bricks Nos. 2 and 3 are referred to as a concluding example; although there is nothing striking about their ordinary refractoriness of cone 29, these bricks give particularly good results in either of the load tests and are known to have given great satisfaction as retort material in an industrial setting.

SUMMARY.

The more important indications of the experimental results reported in Pts. I. and II. of this work may be summarised as follow :—

(1) The information obtained from the ordinary refractory test is not a reliable criterion as to the behaviour of refractory material of the alumino-silicate type under load conditions at elevated temperatures; nor can the cone or temperature at which complete failure under load occurs be accepted as an infallible indication of rigidity at lower temperatures.

(2) Under the test conditions of this work, all the firebrick materials examined exhibit a diminution in the coefficient of thermal expansion under a load of 50 lb. per sq. in. at temperatures below 1,300°; in certain cases as low as 1,000°, but with the majority of materials, 1,200° appears to be a critical point in this respect.

(3) Complete failure under load at high temperatures is preceded by deformation occurring during a more or less extended temperature range.

(4) The rate and amount of deformation (d) under load at 1,350° is related to the time (t) of heat treatment at this temperature by the equation $d=\left(\frac{t}{a}\right)^m$; with the units adopted herein, a value of m greater than unity is an indication that ultimate failure under load results chiefly from the effect of temperature on the property of cohesion; a low value of m accompanies deformation with marked softening or diminished internal friction of the brick substance.

(5) With three experimental clay-grog mixtures, the value of m was lower with the highly grogged bricks than with the bricks of lower grog content or the straight clay bricks.

(6) A classification of firebrick materials, based on their load behaviour at high temperatures, has been suggested and the

wide applicability of the data from the modified Mellor and Moore test, coupled with a *suitably* interpreted result of the 1,350° load test, has been indicated.

The combined data obtained from these two tests should constitute reliable criteria as to the properties of refractory material *at working temperatures*, apart from actual resistance to deformation, *e.g.*, permeability, resistance to abrasion, vibration, gas and slag penetration, etc. This statement, however, is not intended to carry with it any degree of finality.

At this stage of the work, the author desires to express thanks to Mr. C. H. Yeaman, Chief Electrical Engineer of the City of Stoke-on-Trent, for the excellent facilities he has placed at our disposal, both as regards power supply and the loan of certain delicate and expensive apparatus in connection with pyrometric determinations; to the Derbyshire Silica Fire-brick Company for the firing, at their works, of a large number of experimental bricks.; and to Mr. V. Hackney, of the Testing Department of the Central School of Science and Technology, Stoke-on-Trent, for much valuable honorary assistance with the experimental determinations.

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XVII.—An Investigation of the Effects of Load, Temperature and Time on the Deformation of Firebrick Material at High Temperatures.†

A. J. Dale, B.Sc., A.I.C.

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[The term "typical firebrick" is freely used in this paper; it should therefore be appreciated that this term is applied only in a "qualitative" sense.]

Introductory.

In two previous reports,[1] by the present author, results have been presented indicating the behaviour of a wide selection of commercial and laboratory-made firebrick products, under a load of 50 lb. per sq. inch., when subjected to a rise of temperature of 50°C. per five minutes :—

(*a*) Until complete failure occurred.

(*b*) Until 1,350°C. was attained, this temperature being maintained constant for two hours.

The results from the former series of experiments demonstrated that, before complete failure occurs, there exists for all firebrick-material a more or less extended temperature range during which subsidence will take place under a load of 50 lb. per sq. inch. This temperature range was termed the "softening range" but to avoid misconception of the physical nature of the brick at the commencement of this period, the term "subsidence range" is used in this paper.

The second series of determinations involved a consideration of the subsidence occurring under the given load at 1,350°C., a temperature which was, in the majority of cases, well above the lower temperature limit of the subsidence range. The data hence obtained emphasized the importance of the time factor.

Neglecting for present purposes those firebrick refractories with which subsidence at 1,350°C. was of so small a magnitude as to be masked by the expansion of the carborundum thrust rod and supports, it was shown that with a remaining large group of firebricks, the subsidence-time relations under the imposed test conditions conformed to a relation of the type $D=Kt^m$, where $D=$ 'scale' deformation or subsidence, $t=$time and "K" and "m" are constants for a given temperature, "m" having a value less than unity.

In other words, for a group of firebricks including many known to be in demand for high temperature structures in this country, there is a remarkable qualitative similarity in the progress

† Part 3 of the work on this problem.

of subsidence under a load of 50 lb. per sq. inch. at a constant temperature within the subsidence range.

The ultimate chemical composition of these products varied over a relatively wide range, viz., from a SiO_2 content of 71% to, one of 50%, from Fe_2O_3 5% to 0·58% and from alkali (K_2O+Na_2O) contents of 2·7% to 0·58%. We cannot therefore hope to attribute with much success, this similarity in the mechanism of deformation under stress at high temperatures to similarity either in chemical or in physico-chemical composition, nor to such physical similarities at ordinary temperatures as grog contents, gradings or textures. Rather are we forced to seek an explanation in purely physical phenomena and on the field of physical possibilities; attention must ultimately be focussed on the laws governing the deformation or flow under stress of matter in the viscous or/and plastic state.

Theoretical Considerations.

It is indeed remarkable that the fundamental basis of the present day theory of structures is Hooke's Law, propounded as far back as 1676. The law itself deals only with the small elastic deformations which disappear as soon as the load is removed, and it may be written $W= ED$ or $D=K\,W$, where W=stress or load per unit area of material, D=strain or deformation per unit length of material, E (or $\frac{1}{K}$)=a constant for a given material at a given temperature and is termed the modulus of elasticity. Expressed in words, strain is proportional to stress.

No time factor is involved in the above relation, *i.e.*, according to Hooke's Law, the deformation takes place and is completed immediately the load is applied.

Investigation of the behaviour under stress of numerous types of non-metallic and metallic constructional materials has, however, shown Hooke's Law to be either invalid in numerous cases or to have only a very limited range of application. Thus, Walker[2] states the stress-strain relationship for concrete to be represented fairly accurately by an equation of the type $W=KD^n$, where K and n are constants.

Similar equations have been suggested by Bach and Morsch[3]. Nutting[4], working on pitchy materials used for road construction, has demonstrated experimentally the validity of an equation of the type $D=KW^m\,t^n$, where K, m and n are constants, thus giving prominence to the time factor (t). Dickinson and others[5] also emphasise the time factor involved in the tensile deformation of metals and alloys at elevated temperatures. Lamb[6] similarly draws attention to the "creeping" which accompanies the elastic deformation of silica bricks at ordinary temperatures, providing a certain load value is exceeded. Numerous other cases could be cited. Such evidence might be taken to indicate that Hooke's Law is merely a special case of a very general law of the type

$$D=f(t)\,f_1(W)\,f_{11}(T)$$

with the deformation under stress D, proportional to some function of the time t, the stress W and the temperature T.

[Thus, if it be assumed that $D=kt^mW^ne^{bT}$, then, when the constants have values $m=0$, $n=1$, $b=0$, the relation becomes $D=kW$, or Hooke's Law].

The present experimentation was accordingly devised with a view to disclosing the nature of the independent effects of load, temperature and time on the deformation of firebrick materials at elevated temperatures, the indications of previous work[1] being regarded as evidence that the behaviour of a suitably chosen material could be legitimately accepted as qualitatively typical of firebrick material in general.

Experimental Considerations.

Assuming the deformation of firebrick material under load at high temperatures to be proportional to some function of the time t, the load W, and the temperature T,

i.e., $D=f(t)\,f_1(W)\,f_{11}(T)$

it appeared possible, by carrying out a series of determinations in which any two of these three variables, time, temperature and load were maintained constant, to obtain experimental evidence concerning the nature of the function of the third variable. For example, by considering only the amount of deformation occurring under different loads at 1,350°C. during a two hour interval, (*i.e.*, temperature and time constant), a series of determinations under varying loads should expose the individual effect of load on deformation.

Similarly, the independent effect of temperature on deformation should be demonstrated by determining the deformations occurring in a series of experiments at different temperatures with load and time factors maintained constant ; and the nature of the time function by a comparable procedure.

Experimental Method and Apparatus.

For the reasons outlined above the present experimentation involved the continuous recording of the deformation of a typical firebrick material under the following imposed test conditions:

(1) At 1,350°C. under loads of 50, 30, 18 and 4 lb. per sq. inch.
(2) At 1,300°C. under the same load values.
(3) At 1,250°C. under similar load values.

Each determination comprised the heating of a $3\frac{1}{2}'' \times 2'' \times 2''$ test piece, while subjected to the required load, at a rate of 50°C. per five minutes until the desired temperature was attained.

The temperature was then maintained constant for a period of from two to three hours during which time the progress of the subsidence, as indicated by the movement of the cross-wires

placed at the extremity of a magnifying lever arrangement, was recorded.

A detailed description of the apparatus of experiment has previously been published[1] and need not be repeated here.

Precautions were taken to ensure constancy of test piece length and particularly of the area and parallelism of the end faces. The limit of accuracy of work at temperatures around 1,350°C. involving the use of a comparatively large electric tube furnace of the granular carbon resistance type was, of course, appreciated, and every endeavour made to minimise the causes of possible errors.

Experience with this type of furnace has indicated the greatest errors in constant high-temperature work to be due to local overheating of certain parts of the furnace tube, to insufficient control on the temperature variations, and to variations in the furnace atmosphere.

For the work reported herein these errors have been reduced to a minimum by

(*a*) Obtaining the heating effect by current intensity at comparatively low voltage rather than *vice versa*.
(*b*) By use of variable voltage supply and external resistance.
(*c*) By smearing the surface of the heating tube with a wash of low refractoriness.

The temperature itself was recorded by means of a Pt. Pt/Rh couple enclosed in a glazed porcelain sheath and placed so that the hot junction was maintained in close proximity to a centre of one face of the test-piece.

During the constant-temperature heat-soaking period of each test procedure, the furnace was repeatedly searched for temperature inequalities by means of a standardised pyrometer of the disappearing filament type. Additional checks on the comparability of the constant temperature treatments were afforded by the use of cones placed around the test-piece.

Material of Experiment.

The choice of a typical* firebrick material for this work was a point of some considerable importance since considerations of time rendered it impossible to extend this comparatively lengthy series of determinations to more than one product. The choice fell ultimately on a brand of commercial firebricks previously examined and reported upon.†

The dimensions of the bricks supplied for the present work were, however, $9'' \times 4\frac{1}{2}'' \times 3''$ compared with $9'' \times 4'' \times 2{\cdot}2''$ approx. for the sample examined on the previous occasion. This point is mentioned since the results obtained show an appreciable difference

* Typical as regards nature of subsidence under load at high temperatures but not necessarily as regards amount of subsidence. See foreword.
† See Pt. II., pp. 181 *et seq.* Brick No. 14.

in the mechanical properties of the respective samples at high temperatures ; it may, therefore, prove to be a factor of some significance to the firebrick manufacturer, and is considered in a separate report. The chemical and certain physical characteristics of the material of the present experimentation are tabulated below.

Ultimate Chemical Analysis.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O Na_2O
59·17	1·40	33·83	3·52	0·36	0·60	1·62

Specific Gravity and Porosities.

	Apparent % Porosity	True % Porosity	% Sealed Pores	True Sp. Gr.
Interior of Brick ..	21·7	22·4	0·7	2·629
Exterior of Brick	19·3	21·0	1·7	

The density determinations were carried out in triplicate, using paraffin, and the usual precautions taken.

Ordinary Refractoriness—Cone 30.

Texture.

The sample exhibited a vitrified outer skin and a section showed a close-textured exterior portion extending to a depth of from one half to one inch. The interior of the bricks were more open textured and did not show those characteristics of more advanced vitrification evinced by the outer inch.

With all the bricks examined, a certain discontinuity of structure, apparently a making fault, was noticeable at a depth of about $\frac{3}{4}''$ from the surfaces.

Many of the larger particles of a graded grog were "dark-cored."

Selection of the Test Pieces.

The respective differences between the true and apparent porosities of the interior and exterior parts of the brick, (*i.e.*, the sealed-pore values) provide additional evidence of the different stages of vitrification attained by different portions of one and the same brick.

In order, therefore, to eliminate as far as possible errors in this work due to physical differences of test pieces cut from different parts of the brick shapes, all test-pieces were cut from corresponding portions of the bricks.

THE SUBSIDENCES UNDER LOAD AT DIFFERENT TEMPERATURE AND LOAD VALUES.

The rate and amount of subsidence of the experimental material, treated under different temperature and load conditions, is reproduced graphically in Figs. 1. 2 and 3, the ordinates denoting deformations in inches (magnified 16·1 times), the abscissæ indicating temperatures to the desired value and time beyond that point. In each case the almost uniform initial rate of expansion of the test piece, the carborundum thrust rod and supports will be observed (*AB* Fig. 3). In each case also, a definite diminution in the rate of vertical thermal expansion under load is noticeable in the region of 1,050°C. (*B* Fig. 3). No quantitative significance, however, is attached to the varying angle of slope of the expansion portions of the individual curves, since this is, undoubtedly, affected by the variation in length of the hot zone of the furnace during the different determinations.

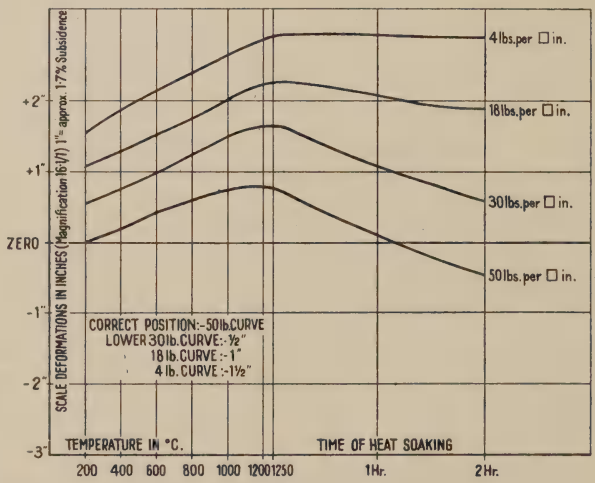

Fig. 1.
Showing progress of subsidence under varying loads at 1250°C.

Fig. 1 reproduces the results of four separate determinations at 1,250°C. under loads of 50, 30, 18 and 4 lb. per sq. inch respectively. The deformation occurring under the last load value was extremely small, and had not amounted to 1/100″ after 2½ hours heat-soaking at this temperature.

Without going into details at this stage, it is obvious from Fig. 1 that load has a considerable effect on the amount of deformation, even at 1,250°C., since the deformation under a load of 50 lb. per sq. inch assumes, after two hours, a magnitude ten times greater than that occurring under a 4 lb. per sq. inch loading.

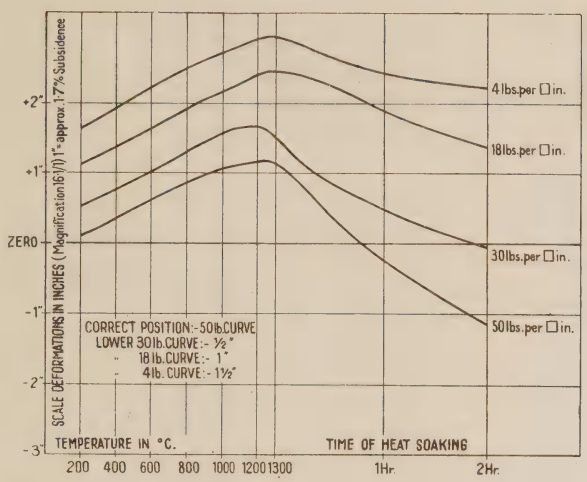

Fig. 2.
Showing progress of subsidence under varying loads at 1300°C.

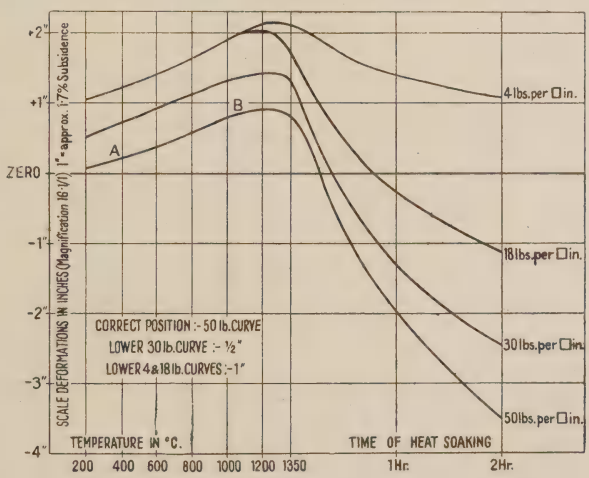

Fig. 3.
Showing progress of subsidence under varying loads at 1350°C.

Figs. 2 and 3 reproduce the rate and amount of deformation under similar loads during heat-soaking periods at the higher temperatures of 1,300° and 1,350°C. respectively.

It is interesting to note that the subsidence portion of all the curves in these three diagrams satisfies an equation of the type

$D = \left(\frac{t}{a}\right)^{m}$* where D and t represent scale deformations and time respectively, and m and a are constants. The values of the constants "a" and "m" which satisfy the various curves are shown in Table 1, together with the percentage subsidences after two hours.

TABLE I. SHOWING VALUES OF CONSTANTS "a" AND "m".

Temperature	1350°				1300°				1250°			
Load in lb. per sq. inch	50	30	18	4	50	30	18	4	50	30	18	4
Value of "a"	13	10	8	468	28	37	98	158	80	100	269	
Value of "m"	0·63	0·55	0·43	0·56	0·64	0·50	0·80	0·63	0·60	0·63	0·65	
% Subsidence	7·31	6·41	5·43	1·40	3·3	2·3	1·52	0·71	1·85	1·44	0·71	0·14

Of the eleven values of "m" given in this table, eight fall between 0·65 and 0·55; furthermore, there is no systematic variation in the values of "m" obtained under different load and temperature values.

It therefore appears that the time-deformation relations of firebrick material under load at any temperature within the subsidence range might be represented by an equation of the type $D = Kt^m$, where m is independent of either temperature or load.

In this case, the numerical value of "m" would seem to be, to some extent, characteristic of the joint physical, chemical and mineralogical properties of the material under examination.

However, the abnormal values of "m" obtained for the 18 lb. loading determination at 1,300° and 1,350°C. prevent the statement of a generalization in this respect.

THE INDEPENDENT EFFECT OF LOAD ON DEFORMATION AT HIGH (CONSTANT) TEMPERATURES.

In Fig. 4, the data from Figs. 1, 2 and 3 are reproduced in a manner intended to give prominence to the effect of load on the magnitude of deformation occurring in a given time (2 hours) at different temperatures within the subsidence range of firebrick material.

The following consideration of the curves of Fig. 4 which depict the deformation-load relations at high temperatures for the typical firebrick material of the present investigation, appears to the author to form a fundamental basis for important generalisations regarding the behaviour of fireclay refractories under load at temperatures within the subsidence range. Referring to Fig. 4,

* Part II, p. 178.

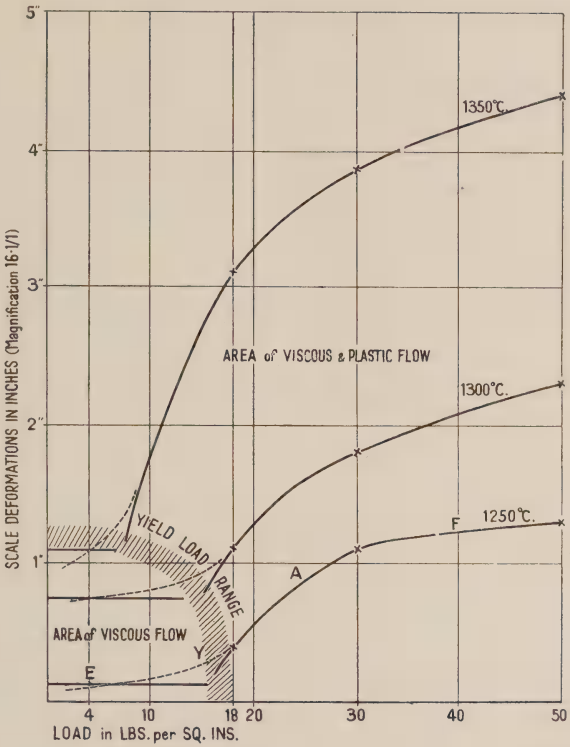

Fig. 4.
Showing effect of load on magnitude of deformation occurring in constant times at the constant temps. shown.

curve EF, which reproduces the deformation-load relations at 1,250°C., shows the undermentioned characterictics :

(*a*) An initial part EY, of relatively small angle of slope, emphasized artificially in the diagram by a horizontal line.

(*b*) A marked increase of slope (*i.e.*, of the ratio, deformation/load, D/W) between load values of 4 and 18 lb. per sq. inch, presumably localised around the point Y. In other words, there is apparently a *yield load value* above and below which the deformation-load relations afford a distinct contrast.

(*c*) A part YA, with the ratio D/W practically constant but having a value much greater than the corresponding ratio for the initial portion, EY.

(*d*) A part AF during which the ratio D/W is undergoing a continuous diminution with increasing loads.

The other curves referring to the load-deformation relations at 1,300° and 1,350°C. respectively exhibit similar characteristics, the

difference being apparently one of degree only.

A joint consideration of the several curves in Fig. 4 indicates that—

(1) For firebrick material, the deformation-load ratio, *i.e.*, D/W, at a given temperature within the subsidence range, undergoes a definite increase during a restricted load range. It is not proposed that this increase in the ratio D/W takes place at an exact load value but rather within a comparatively narrow range of load increase; *e.g.*, with the material under investigation, at from 13 to 16 lb. per sq. inch at 1,250°; or from, say, 4 to 6 lb. per sq. inch at 1,350°C. Such a pressure-range can thus be regarded as a "yield load range," and may possibly constitute a "safe load limit."

(2) The higher the temperature, the lower the value of the "yield load" or "safe load limit."

(3) The higher the temperature, the higher the ratio D/W at any load value, W.

Plastic and Viscous Flow.

An interpretation of Fig. 4 on the above lines brings the problem of the deformation-load relations of firebrick material at temperatures within the subsidence range, into close analogy with the concepts of E. C. Bingham[7] on the laws of plastic and viscous flow of materials at ordinary temperatures. Thus, Bingham has concluded that under ideal experimental conditions at normal temperatures, the pressure-flow relations of a plastic body, *e.g.*, clay in the "plastic" state, paints, etc., are of the general form illustrated in Fig. 5 *b*; a certain pressure, p, being necessary to start the flow, after which, the effect of increasing pressure on flow follows the ordinary linear pressure-flow (viscosity) relations as for true liquids (See Fig. 5*a*), *i.e.*, according to Bingham, the pressure flow relations for a plastic body possess two characteristics:—

(1) A yield load (p, Fig. 5*a*) necessary to start the flow.

(2) A constant angle of slope of the pressure-flow curve, *i.e.*, $V/P\text{-}p$ (Fig. 5*a*).

RELATIONSHIP OF CERTAIN TERMS.

Solids (including Plastic Materials).		*Liquids.*
Rigidity (R)	comparable with	Viscosity.
Mobility (U)	comparable with	Fluidity.
$U = 1/R$		
Yield Value (p), finite		Yield Value, zero.

Referring to Fig. 5*b*, for plastic materials, the rigidity $R = \dot{K}\,\dfrac{P-p}{V}$

The "yield value" p, and the rigidity R, (or its reciprocal, the mobility U), define the working properties of a given material. The results of Ackermann[8], Bleininger and Ross, Trouton and others[9] afford confirmation of the above.

There are differences but distinct analogies between Bingham's results and those from the present series of experiments.

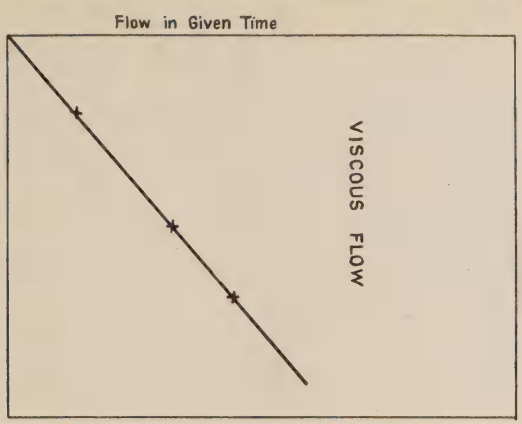

Fig. 5a.

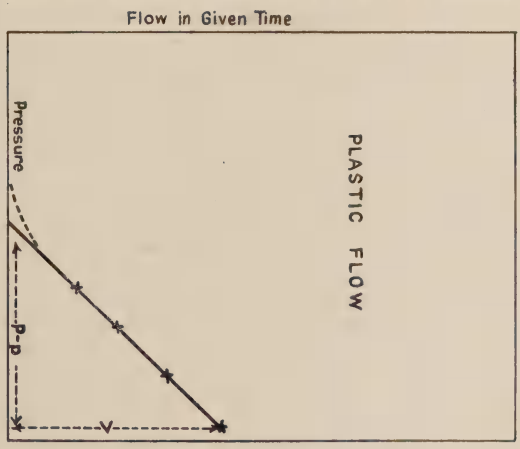

Fig. 5b.

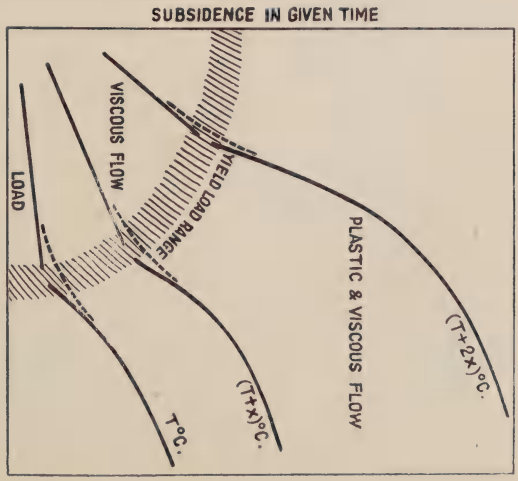

Fig. 5c.

Analysis of the Deformation-Load Relations for Firebrick Material at High Temperatures.

Fig. 5*c*, based on Fig. 4, shows the author's conception of a series of deformation-load relations typical of firebrick material at temperature intervals of x°C. within the subsidence range.

Flow during the initial portion of each curve is considered to be of the purely viscous type; it may be a surface effect.[10] For this initial portion of each curve, if $D=KW$ approx., the value of the constant K increases as the temperature rises.

As the load attains a certain value (yield value), deformation of a more deep-seated origin sets in, this phenomenon agreeing more or less with Bingham's characteristic of plastic deformation (*vide supra*). During the second portion of each curve, deformation is both plastic and viscous.

The ultimate flattening of the curves at still higher loads is, no doubt, the result of an alteration in the texture of the material, *e.g.*, a flattening of the pores[11] accompanied automatically by a bulging of the piece and a corresponding decrease in the initial load on a central cross-section.

THE SIGNIFICANCE OF A MODIFIED MELLOR AND MOORE TEST-RESULT TO THE USER OF FIREBRICK REFRACTORIES.

The modified Mellor and Moore test-result presented in Fig. 6 illustrates the behaviour of the experimental material heated at a rate of 50°C. per five minutes, under a load of 50 lb. per sq. inch, until complete failure occurs. Under this rate of heating, the test piece face temperatures recorded in the diagram are estimated to be approximately 30°C. in excess of the *average* test piece temperature.

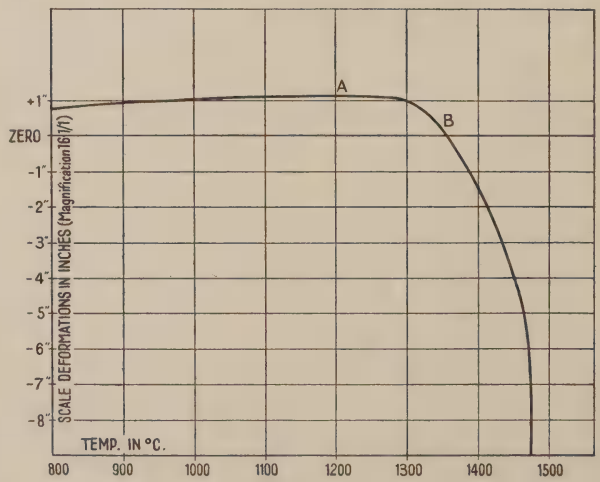

Fig. 6.
Showing progress of subsidence, under 50lb. per sq. in. and a uniform rate of rise of temperature

According to the above consideration of Fig. 4, the part of Fig. 6 to which attention should be directed is the range *AB*. Below a temperature corresponding with *A* (the point at which marked flattening of the curve becomes noticeable, approx. 1,200°C), deformation under loads incurred in ordinary practice will be small. Within the range *AB* (1,200° to 1,350°C. approx., marked acceleration of the rate of subsidence under 50 lb. per sq. inch, occurring around the latter temperature value), deformation both in rate and in quantity is governed by the actual temperature and load values.

Under certain conditions, it may become excessive in both respects. Beyond *B* (1,350°C.) excessive deformation would presumably occur under very low loadings, provided the temperature distribution throughout the brick were fairly uniform. The method of applying a modified Mellor and Moore test-result on firebricks to industrial considerations is therefore made clear.

INDIVIDUAL EFFECT OF TEMPERATURE ON DEFORMATION.

The curves of Fig. 7, also reproduced from the data presented in Figs. 1, 2 and 3, bring out clearly the individual effect of temperature on the magnitude of deformation taking place in constant times and under the given load.

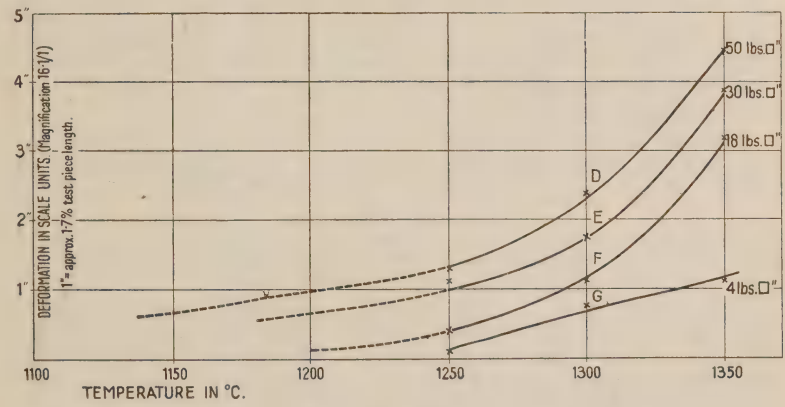

Fig. 7.
Showing effect of temperature on magnitude of deformation occurring in constant times under the constant loads shown.

A consideration of the curves *D*, *E* and *F*. (Fig. 7), which refer specifically to the effect of temperature on the magnitude of the deformation occurring in two hours under loads of 50, 30 and 18 lb. per sq. inch respectively, emphasizes the sensitivity of the experimental material to small changes of temperature, providing the actual temperature exceeds a certain minimum value.

With the material in question, small increases in temperature above 1,300°C. (approx.) would appear to exert comparatively large effects on the resistance to deformation under load (or rigidity),

providing the load exceeds a certain value, in this case somewhere between 4 and 18 lb. per sq. inch.

Although the phenomenon of melting in the strict scientific sense is seldom encountered in ceramic work, these results provide evidence that *for a large class of firebrick material heated under certain load conditions, there exists a comparatively narrow and critical temperature interval below and above which the resistance to deformation under stress affords a marked contrast.*

In the special case examined, reference to Fig. 6 and to the ordinary refractory result (Cone 30) shows this critical temperature interval to be approximately 470°C. below the temperature at which rapid flow occurs under no load and approximately 180°C. below the temperature at which complete failure sets in under the applied test conditions and a load of 50 lb. per sq. inch.

The approximate linearity of curve *G* (Fig. 7) which deals specifically with the effect of temperature on the magnitude of deformation occurring in constant times under a load of 4 lb. per sq. inch is interesting.

It is the type of deformation-temperature relation under loads below the yield value (*c.f.* Fig. 5*c*) one might predict from a consideration of the viscosity-temperature relations, *at high viscosities*, obtained by Field[12] in his work on blast furnace slags. The linearity of *G*, Fig. 7, strengthens the hypothesis previously brought forward in this paper, viz., that under loads less than the yield load, deformation of firebricks material under stress (at temperatures within the subsidence range), is a viscosity effect.

If the data reproduced in curves *D*, *E* and *F*, Fig. 7, be plotted, the logs of the deformations against corresponding temperatures,

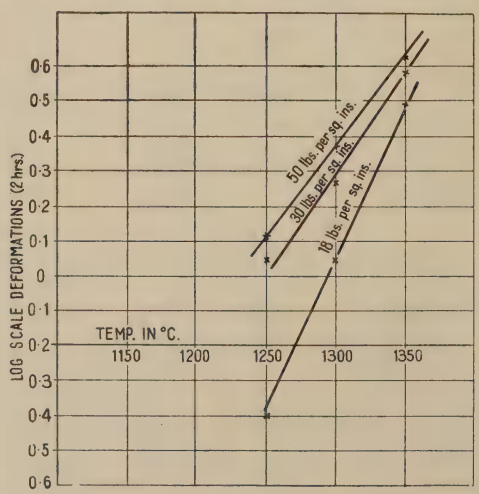

Fig. 8.

the points so obtained fall approximately on a series of straight lines. (see Fig. 8). The relation between deformation and temperature, providing a certain load-value is exceeded, is, therefore, of the exponential type, the deformation occurring in a given time being approximately a logarithmetric function of the temperature, *i.e.*, $D=ce^{bT}$ where D=deformation or vertical subsidence, T= temperature and "c" and "b" are constants for a given load. It might be inferred from Fig. 8 that the value of the "constant" b decreases for increasing loads. A relation somewhat analogous to the above has been brought forward on empirical grounds by English[12], dealing with the temperature-mobility relations of glass.

The establishment of an exponential relation of the above type has a possible important practical application as regards the rate of an initial firing of a setting, say at the end of the "slow firing" period of a retort block.

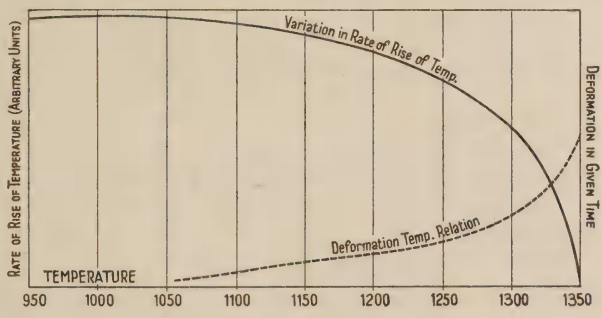

Fig. 9.

Showing theoretical manner in which rate of rise of temperature should diminish during initial firing of firebrick settings, if differential subsidence and straining is to be minimised.

If differential deformation of various stress-bearing portions of a setting is to be reduced to a minimum, if not avoided, the rate of rise of temperature at temperatures above the point corresponding with A (Fig. 6), as indicated by a modified Mellor and Moore test result, should fall off in an exponential manner as temperature increases.

This inference is illustrated in an approximate manner by Fig. 9.

The curves of Fig. 7 also emphasize the necessity for the scrupulous limitation of temperature below a prescribed maximum. Thus, in the case under examination, reference to Fig. 7 indicates that an increase of temperature of only 50°C. above 1,300°C. results in an increase of over 100% in the deformation occurring in a given time (2 hours).

SUMMARY.

The results of an investigation of the independent effects of (*a*) load, (*b*) temperature and (*c*) time on the deformation of a typical firebrick material at temperatures within the subsidence range, have been presented herein.

Evidence has been obtained, that :—

(*a*) (1) The flow of firebrick material under stress at temperatures within the subsidence range is in certain respects qualitatively analogous with the stress–flow relations of "plastic" materials at ordinary temperatures.

(2) For any given temperature within the subsidence range, a *yield load range* exists.

(3) At loads below this yield load range, flow under stress, is probably a viscosity effect.

(4) At loads immediately above the yield value, flow is presumed to be both viscous and plastic. During this period, the ratio D/W is large compared with the corresponding ratio at stress values below the yield value.

(*b*) (1) The higher the temperature the lower the value of the yield load.

(2) Providing a certain temperature is exceeded, the deformation temperature relation for firebrick material is an exponential one, *i.e.*, $D=ce^{bT}$, where c and b are constants for a given loading.

(3) Below this temperature the deformation-temperature relation is approximately a linear one, *i.e.*, $D=kT$.

(*c*) The deformation-time relation previously put forward, $D=kt^m$, holds for different load and temperature values under the test conditions.

Practical indications have been obtained with regard to

(1) The regulation of the rate of rise of temperature during the initial firing of a firebrick setting.

(2) The need for accurate limitation of temperature below a prescribed maximum, dependent on the material and on the load to be sustained.

(3) The general method of applying a modified Mellor and Moore load-test result to industrial considerations.

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XVIII.—Some Fallacies to be Avoided in the Standardisation of any Method of Testing the Load-Bearing Capacities of Refractories at High Temperatures; and a Suggested Method for Standardisation.

A. J. Dale, B.Sc., A.I.C.

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Objects of the Present Report.

The objects of this paper are to summarise the different methods devised to test the load-bearing capacity of refractory materials at high temperatures, to consider critically these methods in the light of recent work and hence to indicate a load-test procedure which, in the present state of our knowledge, appears least likely to yield anomalous results. The theme of this report is developed purely from the testing viewpoint.

Aim of a Load Test.

For the present purposes, it is assumed that the primary aim of a high temperature load test is to enable an estimate to be made, quickly, simply and cheaply in the laboratory, of the resistance of a given material towards deformation or subsidence under certain conditions of loading and *uniform* temperature encountered in carbonising plants and other high temperature structures.

Limited Value of an Ordinary Refractory Test Result.

There are two phenomena which tend to reduce the value of the ordinary refractory test result as a forecast of the resistance of refractory material towards deformation in industrial practice where these joint conditions exist—load and *uniform* high temperature. These two phenomena are:—

(1) Progressive softening or/and diminution of cohesion begins at temperatures which are in some cases very much below the ordinary refractory-test result.

(2) The temperature interval between the ordinary refractory test result and the temperature at which subsidence under load commences is variable and depends on the nature of the material itself.

Proof of these two points will be found in the results obtained with thirty-six products examined by the present author[19] and in the following collection of results on Continental products recently published by Hirsch[1].

TABLE I.

Lab. Mark	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Chemical Analysis SiO_2 ..	83·92	77·54	72·99	66·85	62·01	60·68	56·59	56·01	54·45	54·28	53·88	52·08	52·06	48·30
Al_2O_3 ..	15·08	18·65	23·47	28·81	36·67	37·53	40·64	41·34	43·04	42·65	43·02	45·06	46·45	42·67
Fe_2O_3 ..	0·58	1·42	1·28	2·25	0·80	1·49	2·16	1·84	1·64	2·30	2·00	2·18	1·40	5·29
Ord. Refractoriness in Cones	29/30	32	31	30	32	33	34	34	34	34	34	34/35	35	31/32
Commencement of Subsidence under 2 kg. per sq. cm. .. .. (28 lb. per sq. in.)	1290°	1225°	1125°	1240°	1325°	1390°	1390°	1300°	1250°	1230°	1225°	1285°	1250°	1175°
Rapid Subsidence commences at	1370°	1525°	1525°	1425°	1575°	1650°	1600°	1575°	1550°	1410°	1500°	1620°	1510°	1455°

According to these data, deformation under low loads may commence hundreds of degrees below the "fusion" point as shown by the ordinary refractory-test procedure.

Methods intended to Estimate Resistance to Deformation at High Temperatures.

Apart from the ordinary refractory test, the typical methods which have been applied to the above-mentioned purpose can be classified as follows:—

Method 1. A simulation of the ordinary cold-crushing test. The refractory is heated to the desired temperature, the pressure is applied quickly and the test result is reported in lb. per sq. in. (or kg. per sq. cm.) required to cause collapse.

The method appears to have been used first by Gary[2]; it was later adopted by Le Chatelier and Bogitch, and by Bigot, and further developed by Bodin[3].

It is obvious that this method must fail to have much practical significance when applied to many fireclay products at temperatures in excess of approximately 1,200°C. Owing to the progressive softening of many firebricks at these temperatures, the supporting structure becomes, physically speaking, comparable with viscous fluids such as treacle, softened glass, etc. It would hardly be possible to attach any practical importance to a report that the crushing strength of a column of treacle is, say, 150 lb. per sq. in.; the column might support this loading for a fraction of a second, but we know that continued deformation would occur under a $\frac{1}{4}$ ounce per sq. in. loading if sufficient time were allowed.

Method 2.

A hot modulus of rupture test. This procedure involves supporting the brick at its ends and heating it to the required temperature; a load sufficient to cause fracture is then rapidly applied to the centre of the brick. McGee[4] restricted the procedure to silica products, but if the method is applied to fireclay products, as it was by Hartman and Koehler[5], the above criticism of Method 1 applies, and the results lose much of their significance.

Method 3.

The method introduced by Haereus, who determined the rate of penetration of a loaded iridium rod into the test material heated to the desired temperature. This process of experimentation has recently been modified by Rengade and Desvignes[7] who determined the size of the indentation produced in ten minutes by a loaded right-angled cone of Acheson graphite.

The principle of these methods is somewhat similar to that of the Vicat needle test for the consistency of clays and cements, and also to the Brinel hardness test for metals, as modified by Ludwik[8]: while the either of the two former methods may provide useful indications with fairly homogeneous materials, it is doubtful if

reliable results will be obtained with commercial refractory products, carrying fairly high grog contents or possessing textures which vary considerably from the exterior to the interior. The results must in such cases be regarded as typical only of the surface of the product and not of the brick or shape considered as a whole.

Method 4.

A determination of the resistance to tensile elongation at high temperatures. This method was applied by Bleininger and Teetor[9], who used a static tensile loading, to porcelain bodies and by Brown[10], to specially made clay pieces.

Tarrant[11] also emulated the ordinary tensile test procedure (rapidly applied loading) on unfired products, but his results are difficult to understand.

Method 5.

This method, originated in America by Parker[12], was developed by Bleininger and Brown, Sieurin and Carlsson, Shaw and others[13], and recently standardised in the States as a means of testing the load-bearing capacity of refractories at working temperatures[14]. The standardised procedure as applied to the better grade firebricks consists of heating a full sized brick at a fixed rate and under a static load of 25 lb. per sq. in. until a temperature of 1,350°C. is attained. The temperature is then maintained constant for 1½ hours and the test result is reported as the percentage subsidence caused by this treatment. The test, therefore, aims at classifying refractories in order of merit (as regards resistance to deformation), according to the amount of subsidence brought about by a fixed load and heat treatment; it is, however, the author's opinion that the standardisation of such a procedure is based on certain fundamental fallacies, discussed later in this report.

Method 6.

The Mellor and Moore high-temperature load test, as used hitherto in this country[15]. This test-result is reported as that cone at which collapse occurs of a 3½in.×2in.×2in. test-piece, subjected to a static load (usually 50 lb. per sq. in.), and a constant rate of rise of temperature. The method has been adopted by Mellor and Emery, Bradshaw and Emery, Kowalke and Hougen, Griffiths and others[15]; but Mellor and Emery[16] have stated that in certain cases anomolous results may be obtained.

Method 7.

The modified Mellor and Moore test; with the discovery of materials which are capable of withstanding pressure without deforming up to temperatures of 1,700°C. or above and which are therefore suitable for supporting and applying the load to test material, this method is a logical development of Method 6. In

this modified test, a complete record is made of the progress of subsidence under load from that temperature at which vertical thermal expansion ceases up to the temperature at which rapid or complete failure occurs. The method is, therefore, almost identical with that adopted by Mellor and Moore, but the test result is presented in the form of a continuous curve. This modified procedure has recently been applied in Germany by Endel and Steger, Hirsch, Hirsch and Pulfrich and Steinhoff,[17], in America by Wilson[18], and by the present author in this country[19].

In the above review, Methods 1, 2 and 3 have been shown to be unsuitable for adoption as a standardised means of comparing the load-bearing capacities of firebricks at high temperatures. Method 4 is, as yet, comparatively unexplored in connection with commercial refractories and Method 6 has been shown by Mellor and Emery to be capable of yielding anomalous results in certain cases. It therefore remains to consider the relative merits of the standardised American method and the modified Mellor and Moore procedure, and for this purpose a detailed consideration appears essential.

Mechanism of the Deformation of Firebrick Material under load at High Temperatures.

Previous work[19] has shown that it is of prime importance for the user and the manufacturer* of firebrick products to realise the practical significance of the difference between the behaviour of two types of matter—solids and fluids—subjected to stress or load. This difference was exemplified by Maxwell[20] as follows:—He says—

> "A tallow candle is much softer than a stick of sealing wax ; but if the candle and the stick of sealing wax are laid horizontally between two supports, the sealing wax will in a few weeks in summer, bend under its own weight, while the candle remains straight. The candle is, therefore, a soft (plastic) solid, while the sealing wax is a very viscous liquid."

The parenthesis is due to Bingham, who, as the result of an exhaustive consideration of the subject[21], concludes that the significant practical difference between a plastic material (a solid) and a viscous material (a fluid) is this:—a plastic body can resist a load up to a certain value—the yield value—without undergoing permanent deformation, while a viscous body will flow or deform under loads, no matter how small they may be. In other words, we should build our structures with plastic materials and keep the load below the yield value, provided of course, that the above differentation is valid.

We are now in a position to apply the above distinction between plastic and viscous deformation to the present consideration. If, at a given temperature, say 1,300°C., the supporting

* A report intended to show the value, to the manufacturer, of the modified Mellor and Moore load test, is now in the course of preparation.

structure of a firebrick consists of a certain amount of solid (or plastic) material embedded in a viscous matrix, deformation will occur under a load which is below the yield value for the solid portion, until the viscous portion is squeezed out into the pore-spaces; the solid (plastic) particles will then take up the load; at this point, provided the applied load is less than the yield value of the solid particles, deformation will slow off, and may cease, and the future behaviour of the material under the given temperature and load conditions will be characterised by relative freedom from deformation. How does this idea fit in with actual results? An investigation has been carried out to evaluate the effects of time, temperature and load on the deformation of firebrick material at high temperatures and the results obtained have been presented in a previous paper (see p. 199.) These results leave little ground for doubt that the effect of increasing load on the deformation, at an elevated temperature, of this class of material is of the general form shown in Fig. 1.

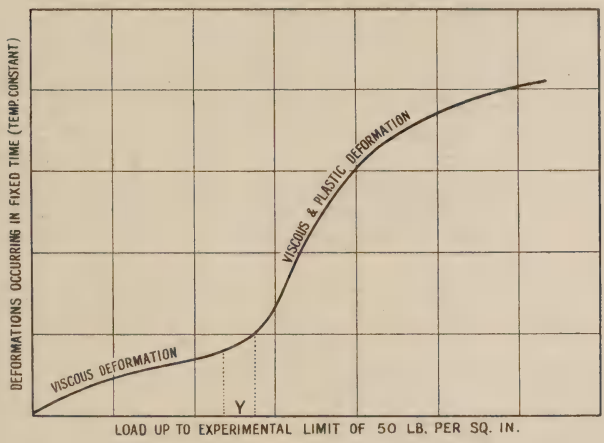

Fig. 1.

Around a certain load value, (Y, Fig. 1,) a marked increase takes place in the amount of deformation occurring in a given time. It is, therefore, presumed that under loads below Y lb. per sq. in., the deformation results from a squeezing out of the viscous portion of the supporting structure, and diminishes in velocity as the solid (or plastic) portion takes up the load. At loads above Y, however, deformation of both viscous and plastic constituents is occurring.

We might further prophecy that the yield load, Y, constitutes a kind of safe load limit at the temperature to which Fig. 1 refers; and providing the temperature is not too high, although a firebrick material undergoes viscous deformation, it may give satisfactory

use as a load-carrier at high temperatures if (*a*) the actual load is below the yield value of the solid portion of the supporting structure; (*b*) the amount of viscous matter in the supporting structure is not too great at the temperature of use. On this reasoning, any standardised high-temperature load test method should take into account the two possibilities—viscous and plastic flow.

THREE FALLACIES IN THE AMERICAN LOAD-TEST METHOD.

The above interpretation of the mechanism of the deformation of refractories under load at high temperatures suggests that any standardised test method is wrong if it involves merely one determination of the deformation occurring

(*a*) In a specified time.
(*b*) Under a specified loading.
(*c*) At a specified temperature.

(*a*) That the specification of a definite time may be fallacious has already been proved (see p. 178).

(*b*) The fallacy of prescribing a definite load for a standardised constant temperature-time-load test is connected with the fact that if the specified load happens to be greater than the yield value (*vide supra*), the resulting deformation may be out of all proportion to that which would occur under loadings less than the yield value.

To elucidate this section of the argument and at the same time to provide visual evidence of the manner in which a constant temperature-time-load test result may lead to a misinterpretation of the relative values of firebricks from the industrial load-bearing point of view, the following experimental results* are quoted. Two firebricks, Nos 1 and 2, were examined at 1,350°C. under a load of 50 lb. per sq. in.

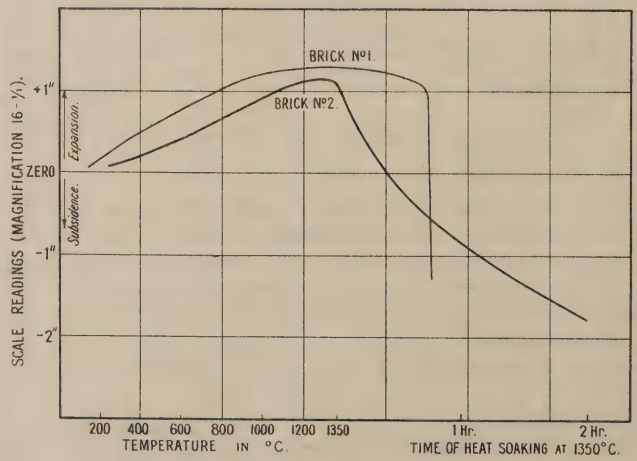

Fig. 2.

* Others are available.

The curves 1 and 2 of Fig. 2 depict their respective behaviours under this treatment, Brick No. 1 collapsing after $\frac{3}{4}$ hour.

The net result of these two tests would be reported as follows:

Brick No. 1 collapsed during the two hours load treatment at 1,350°C.

Brick No. 2 subsided 4·86% during the two hours load treatment at 1,350°C.

The impression gained from such a result is that Brick No. 2 is preferable to Brick No. 1 for high temperature load service. Actually, on the interpretation of the mechanism of the deformation of firebricks at high temperatures summarised above, the only rigid conclusion to be drawn from these two results is that the yield value of Brick No. 1 is lower than 50 lb. per sq. in. at 1,350°C. The actual state of affairs is more clearly brought out by the modified Mellor and Moore test result on these two products, shown in Fig. 3, coupled with an examination of the pieces after testing. While Brick No. 2 is undergoing deformation, probably of the viscous type, at a furnace temperature of 1,150 to 1,200°C., the viscosity of the stress-bearing structure of brick No. 1 is sufficiently high to withstand deformation up to a furnace temperature of about 1,300°C.

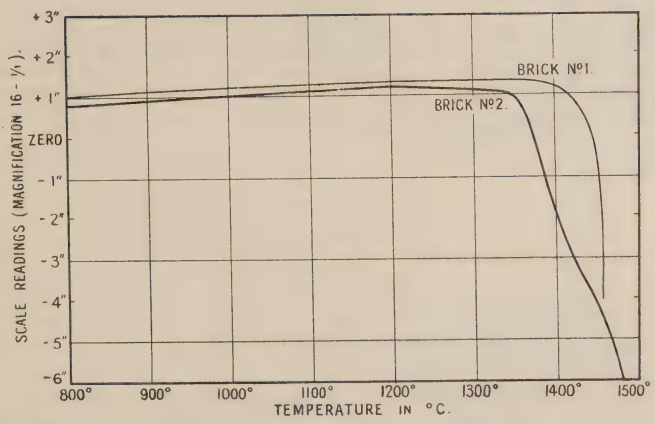

Fig. 3.

Under the moderate loadings encountered in many branches of industrial practice, we would, therefore, expect brick No. 1 to be more stable mechanically than brick No. 2, a conclusion diametrically opposed to the indications of the constant-temperature load test. It should be added here that acceptance of the possibility of two distinct types of flow of firebrick material at high temperatures, with the corresponding acceptance of the "yield value" criterion of plastic flow, also constitutes an argument against the formulation of a specification based only on the actual temperature

(or cone) of rapid collapse under a given load and rate of heating.

The possibility of an anomalous result from the *ordinary* Mellor and Moore load test is explained. Such an anomalous result has already been detailed by Mellor and Emery[16], who showed that a certain firebrick, widely used in gas retort construction, failed completely without warning at cone 3 (1,140°C., 2,084°F.) under a 50 lb. per sq. in. loading, although the brick stood up to cone 29 in the ordinary refractory test. By reasoning similar to that used above, the "yield value" differentiation between viscous and plastic flow explains the apparent anomaly.

(*c*) The third fallacy in the American standardisation is the specification of a fixed temperature of testing. In connection with the effect of temperature on viscous and plastic deformation, the following contribution by Lowry to a metallurgical discussion[22] is relevant and comprehensive. Prof. T. M. Lowry, quoting well-known authorities, says:—

> "In most cases, there must be a considerable range of temperature below the freezing point within which an overcooled liquid has a higher degree of fluidity than the crystal. When, however, you pass to lower temperatures, then you get to the state that Sir George Beilby has postulated, where the amorphous (viscous) phase has increased in rigidity very much more quickly than the crystal (plastic) and finally is a far more rigid material. My conclusions are, therefore, exactly those of Sir Alfred Ewing, namely, that near the melting point, you would expect the glassy phase to be more fluid than the crystal, whilst at lower temperatures you would expect the opposite to be the case. These relations may be illustrated diagramatically as follows" (Fig. 4). (The parentheses have been inserted by the present author.)

This reasoning applies qualitatively to the effect of tempera-

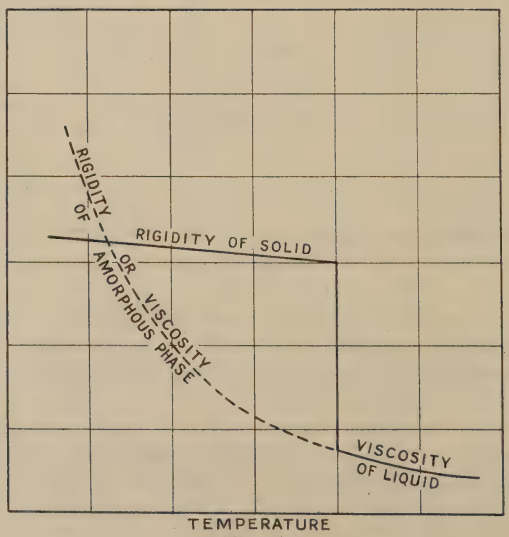

Fig. 4.

ture on the flow of firebrick material under stress at temperatures at which variable amounts of viscous fluid (glassy material) and plastic solid (*e.g.*, crystalline material) may constitute the supporting structure, according to the specific physicochemical nature of the material.

Thus, referring to Fig. 5, the respective behaviours of such material under load at any of the three temperatures T_1, T_2 or T_3 might be expected to be entirely different, and it would be futile to attempt generalisation from the result of any single pressure-deformation test performed at *one* of the three temperatures.

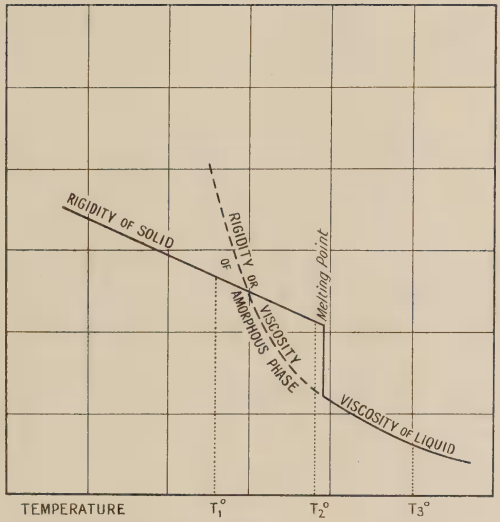

Fig. 5.

SUMMARY.

It has been suggested in this paper that methods which involve rapid application of load are unsuitable as standardised methods of testing the load-bearing capacities of refractory materials at high temperatures; furthermore, methods which require the penetration of loaded rods into the material are also of questionable value. It has also been suggested that any method of testing the load-bearing capacity of firebrick material at high temperature is to be avoided, from the standardisation viewpoint, if it involves merely *one* determination of the amount of subsidence at a fixed temperature and under a fixed load. The results from such a test will not necessarily place the materials in order of merit from the practical load-bearing point of view.

It has, furthermore, been pointed out that the arguments leading to the above conclusion also indicate that any high temperature load-test on fireclay products which involves merely

the recording of the temperature (or cone) at which collapse takes place, under a fixed load, and constant rate of rise of temperature, may also yield anomalous results.

A SUGGESTED STANDARDISED METHOD OF TESTING THE LOAD-BEARING CAPACITY, AT HIGH TEMPERATURES, OF FIRECLAY PRODUCTS.

For the completion of the objects of the present report, the author would suggest, taking into account the experimental and theoretical points already discussed[19], that *the most satisfactory standardised high temperature load-test method for fireclay refractories should involve the continuous recording of the progress of subsidence under a static loading and a uniform rate of rise of temperature.*

As regards the specification of details, the preceding arguments and the results to which reference has been made, suggest the necessity, in the case of fireclay products, for two separate modified Mellor and Moore tests under different static loadings.

(1) One under a relatively high load, say 50 lb. per sq. in. intended to evaluate the tendency of the given material towards viscous deformation at comparatively low temperatures and towards plastic deformation or failure resulting from loss of cohesion at higher temperatures.

(2) A second test under a comparatively low loading, say 10 lb. per sq. in. to afford evidence of the absence of marked "plastic" deformation (*i.e.*, deformation or failure resulting from a loss of cohesion) under moderate loadings up to maximum working temperatures.

The most informative interpretation of the results from these tests will then demand a consideration of

(*a*) the temperature at which subsidence becomes apparent;
(*b*) the temperature at which marked acceleration, if any, in the rate of subsidence occurs;
(*c*) the subsidence ranges;
(*d*) the effect of load on the temperature extent of the subsidence range;
(*e*) the appearance of the pieces after testing.

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XIX.—The Heat-Insulating Efficiencies of some Diatomaceous Earth Products and Slag Wool.

By A. T. Green and H. Edwards.

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Introduction.

In a recent paper by one of the authors[1], the thermal conductivity and some other properties of two commercial heat-insulating materials were defined. This paper, also, mentioned a suggestion made by Hutton and Beard[2] in 1905, concerning the placing of a layer of low-conducting material between the exterior casing and the interior lining of a kiln, furnace, oven or retort, as means of reducing the loss of heat by way of the walls. The use of insulating material in this manner is becoming general. However, little experimental work has detailed the effects of such an interposition on the temperature gradients within a firebrick wall, the hot face of which is maintained at certain high temperatures. The present paper deals with this aspect of the subject, and from the results so obtained, the approximate heat-insulating efficiencies of the various materials used, have been computed. Besides these results, other data concerning the structural efficiencies of the various materials have been obtained.

The Materials of Experiment.

Diatomaceous products and slag wool formed the principal materials of experiment. Two different varieties of the former—the one, a pure earth containing 93 per cent. of SiO_2; the other, a very impure product, containing a considerable amount of clayey matter and iron oxide, were investigated. The purer material, obtained from California, was used in two different forms, viz., (*a*) as a powder, packed to a consistency of (1) 5 lbs. per cubic foot (Material A, see Table 1) and (2) 22 lbs. per cubic foot (Material B); (*b*) as a slab (Material C). This slab was not a fired product, but a piece cut from the original deposit to the dimensions $8{\cdot}6'' \times 4{\cdot}2'' \times 2.5''$. In such a state, this material is supplied to industry. The slab, which was very light, and contained the usual cellular structure of diatomaceous products, also showed a defined lamellar appearance. This fact is of particular significance, since in the experiments when heat was applied to one face of the material, the laminations of which were perpendicular to the direction of heat flow, splitting occurred along three or four such lamellar planes. The production of this splitting affects to some degree the insulating property and also the mechanical strength of the slab.

The powder was obtained from the same deposits as the slab. The grains of this powder possess the same cellular structure as the slab material. This pure material maintains its porosity in

nature and in quantity, at a temperature of, at least, 1,200°C. Other properties of these materials are given in Table 1.

The second variety of diatomaceous earth (Material D) was in the form of a brick of original dimensions $9{\cdot}4 \times 4{\cdot}8 \times 2{\cdot}8$ which had been moulded in the semi-plastic state and fired to a low temperature in the region of 800°C.

In the insulating tests the impure diatomaceous material D was in one experiment subjected to a face temperature of 1,100°C. Definite signs of warping were noted, suggesting incipient fusion. With the object of limiting the safe temperature of practical use, pieces of this material were heated, for various periods of time, to different temperatures, and the change in the nature and quantity of porosity, together with changes in the appearance were noted. These are tabulated in Table 2.

From the observations it seems definite that the safe limit for the hot face temperature of this insulating material D is in the neighbourhood of 1,000°C.

Slag wool (Material E), is a fibrous material which had been made by the action of steam on blast furnace slag. The nature of the porosity of such a material is very different from that which obtains in diatomaceous earth products. Comparatively speaking, the air spaces are considerably larger in the slag wool and consequently, it may be expected that its insulating capacity will be less than that of diatomaceous earth products. Experiments were carried out to determine the temperature at which slag wool loses its fibrous structure. Samples were heated to temperatures ranging from 500°C. to 900°C. After treatment at 650°C. for 2 hours the slag wool showed no signs of disintegration. The same treatment at 700°C. produced evidence of the breakdown of the structure, while such a breakdown was realised by treatment at 750°C. and 800°C., some powder being formed. This defines the statement that slag wool cannot be used successfully for any length of time at temperatures exceeding 700°C.

Method of Measuring the Insulating Capacity.

As in the experimental determination of thermal conductivity[3], a wall of nine bricks was erected with a central brick A as the test brick (Fig. 1). Thermocouples had been placed in the interior of this brick at C and D, by way of holes $\frac{3}{16}''$ in diameter, which had been drilled. C was at a distance of 5·2 cms. from the hot face B (Fig. 1), and D was 5·1 cms. (2″) from C. The hot face B was raised to a constant temperature (*i.e.*, 1,037°, 1,153° or 1,270°C.) in about $1\frac{1}{2}$ hours, by means of the furnace described in a previous paper[3], and maintained at this temperature for 7 or 8 hours. This hot face temperature was measured by means of a thermocouple F, luted to the centre of the face of Brick A. The temperatures at the isothermal planes represented by the vertical planes C and D

TABLE 1.

Material	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	CaO	App. Sp. Gr.	Porosity Apparent	Refractory Test
A	92·70	—	0·88	4·46	0·44	0·08	96·2	Cone 32 (1710°C.)
B	—	—	ditto	—	—	0·34	84·3	ditto
C	—	—	ditto	—	—	0·46	78·7	ditto
D	75·17	0·99	5·56	11·33	1·54	0·53	76·5	Cone 7 (1230°C.)
E	30·92	0·56	0·47	24·70	35·62	0·34	88·1	Cone 07A (960°C.)*

TABLE 2.

No.	Treatment of Piece	% Apparent porosity after treatment	Remarks on appearance, etc.
1	Piece heated from ordinary temperatures to 700°C. in 3 hours. Maintained at this temperature for one hour.	75·3	Colour as in the original piece.
2	Piece raised to 800°C. in 4 hours, Maintained at this temperature for one hour.	75·3	Colour as in the original piece.
3	Piece raised to 900°C. in 5 hours. Maintained at this temp. for 2 hours.	74·3	Colour the same as in the original material. Appears however to be not so friable.
4	Piece raised from ordinary temp. to 1050° C. in 2 hours and then removed. Atmosphere of kiln somewhat reducing.	70·4	Colour darkened considerably. Certain amount of fusion obvious. Nature of porosity much altered.
5	Piece raised to 1150°C. in 3 hours. Piece then removed from furnace. Atmosphere as in 4.	69·2	The effects noted in 4 carried on to a greater degree.

*For this test, pulverized slag wool was mixed with dextrine, dried, etc., and the test carried out on such a test piece. There were no very definite indications of fusion, although the test piece apparently squatted in a manner similar to ordinary fireclays.

(referred to as isothermal planes 1 and 2 respectively) were measured, at intervals, over the period of experiment. The data, so obtained, can be used in the calculation of the temperature diffusivity, and consequently, the thermal conductivity of the brick. Its particular use in the present connection, however, as will be readily appreciated later, is to provide a basis for the comparison of the insulating capacity of the various materials of experiment. The data for the rate of rise of temperature at the two holes C and D (isothermal planes 1 and 2), for this normal brick are reported in the results (Tables 3, 4 and 5 and Figs. 2, 3 and 4) for Material F.

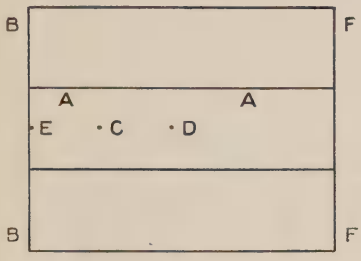

Fig. 1.

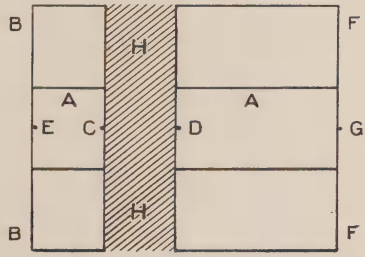

Fig. 1A.

The bricks forming the wall were next sawn through by way of the isothermal planes C and D (*i.e.*, by way of planes through C and D parallel to the hot face). The distance of 2″ between the planes C and D was maintained throughout all experimental work; the intervening space being filled with the various insulating materials, in turn, Fig. 1A shows the arrangement of this apparatus. As in the foregoing experiments with the normal firebrick, the hot face temperature was obtained in about $1\frac{1}{2}$ hours, and the rates of rise of temperature at the planes C and D (Isothermal Planes 1 and 2), determined over the period of experiment.

Table 1 shows the analyses, apparent porosities and refractory tests of the insulating materials used.

Results.

Tables 3, 4 and 5 and Figs. 2, 3 and 4, show the rate of rise of temperature at the 1st and 2nd isothermal planes (*i.e.*, at C and D respectively, see Figs. 1 and 2), for the three hot face temperatures used.

In addition to these results, the temperature of the exterior face F was measured by a couple at G, in the case of the diatomaceous earth powder, *i.e.*, materials A and B. The values of this temperature, at the end of eight hours from the commencement of the run are reported in Table 7.

Discussion of Results.

The graphs of Fig. 2, 3 and 4 show, at a glance, the great effect of the insulating materials on the temperature gradient within the brick wall.

TABLE 3.

Hot Face Temp. 1,037°C. Time taken to reach this temp. 1½ hours.

Time from Commencement of Experiment in Hours	Temperatures of 1st and 2nd Isothermal Planes in °C.											
	Material A		Material B		Material C		Material D		Material E		Material F	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
2 ..	740	—	700	—	723	—	710	—	632	—	—	—
3 ..	860	—	878	—	853	—	832	—	740	—	—	—
4 ..	885	155	878	120	881	125	864	160	804	137	—	—
5 ..	900	184	881	150	881	150	870	190	821	168	560	220
6 ..	905	208	882	180	878	170	882	210	840	193	594	275
7 ..	906	228	896	198	886	188	882	227	841	216	621	310
8 ..	902	240	896	210	896	200	884	240	844	230	642	334
9 ..	—	—	—	—	898	210	882	250	—	—	—	—

TABLE 4.

Hot Face Temp. 1,153°C. Time taken to reach this temp. 1½ hours.

Time from Commencement of Experiment in Hours	Temperatures of 1st and 2nd Isothermal Planes in °C.											
	Material A		Material B		Material C		Material D		Material E		Material F	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
2 ..	796	—	876	—	860	—	818	—	682	—	—	—
3 ..	908	—	990	—	968	—	933	—	868	—	—	—
4 ..	1016	—	1016	—	996	137	961	173	916	157	—	—
5 ..	1000	196	1031	180	1017	174	976	212	928	205	633	282
6 ..	1008	235	1035	206	1008	200	990	241	945	232	672	332
7 ..	1010	252	1037	230	1025	220	997	268	945	252	704	370
8 ..	1016	268	1035	249	1023	238	997	279	950	270	726	394
9 ..	—	—	—	—	1021	245	987	290	—	—	—	—

TABLE 5.

Hot Face Temp. 1,270°C. Time taken to reach this temp. 1½ hours.

Time from Commencement of Experiment in Hours	Temperatures of 1st and 2nd Isothermal Planes in °C.											
	Material A		Material B		Material C		Material D		Material F			
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd		
2 ..	1003	—	983	—	1000	—	898	—	—	—		
3 ..	1089	—	1120	—	1080	—	1063	—	—	—		
4 ..	1105	212	1137	—	1110	196	1087	212	—	—		
5 ..	1124	254	1150	—	1112	226	1097	251	698	332	—	
6 ..	1127	278	1145	259	1122	250	1097	284	743	385		
7 ..	1124	305	1153	284	1120	273	1100	315	776	427		
8 ..	1134	330	1153	300	1122	286	1110	336	804	455		
9 ..	—	—	—	—	1125	294	1110	355	—	—		

TABLE 6.

MATERIAL E.

Hot Face Temperature 778°C. Time taken to reach this temp. $1\frac{1}{2}$ hours.

Time of Commencement of Experiment in Hours	Temperature	
	1st Plane	2nd Plane
2	466	—
3	603	—
4	630	82
5	639	107
6	650	120
7	652	133
8	650	142
9	—	—

TABLE 7.

Material	Temperature of Exterior Face of the Wall at end of eight hours from commencement of experiment, for the Different Hot Face Temperatures in °C.		
	1037°C.	1153°C.	1270°C.
A	58	68	87
B	55	66	82

A study of Tables 3, 4, 5 and 6, or Figs. 3, 4 and 5, indicates that with materials A, B and C an approximately constant temperature, at isothermal plane I, is obtained after about $4\frac{1}{2}$ hours from the commencement of the experiment; with material D, this time is roughly 5 hours, and with material E, $5\frac{1}{2}$ hours. Approximately, then, an average of the temperatures reported for the times, 6, 7, 8 and 9 hours will give the equilibrium temperature for plane I, obtained by using the various insulating materials. Now, since the thermal conductivity of the brick material of the wall can be computed from the data of material F in Table 3, 4 and 5 together with a distance factor, it is easy to calculate from the elementary equation of thermal conductivity, the amount of heat passing through each square cm. of area of the isothermal plane I per second, for each

insulating packing when equilibrium conditions exist between the hot face and isothermal plane I. The computed values of the thermal conductivity of the brick in C.G.S. units are, at 800°C., 0·00116; at 900°C., 0·00126; at 1,000°C., 0·00136; at 1,100°C., 0·00147; at 1,200°C., 0·00160. It may be mentioned here that such values are decidedly lower than those obtained for well-burned Stourbridge firebricks. The computed amounts of heat passing through the isothermal plane I per sq. cm. per second, under the varying conditions of experiment are reported in Table 8. Attention is called to the fact that the result reported for material B at the hot face temperature 1,037°C. appears to be inaccurate, and may be a mal-observation.

TABLE 8.

Hot Face Temp.	Amount of Heat passing through 1 sq. cm. of isothermal plane I per second in calories, with the different packings, after an approximate equilibrium has been set up between the hot face and isothermal plane I.					
	Material A	Material B	Material C	Material D	Material E	Material F
1037°C	0·0347	0·0362	0·0362	0·0399	0·0494	0·0868
1153·C.	0·0398	0·0335	0·0370	0·0455	0·0574	0·1020
1270°C.	0·0442	0·0381	0·0461	0·0508	—	0·1220

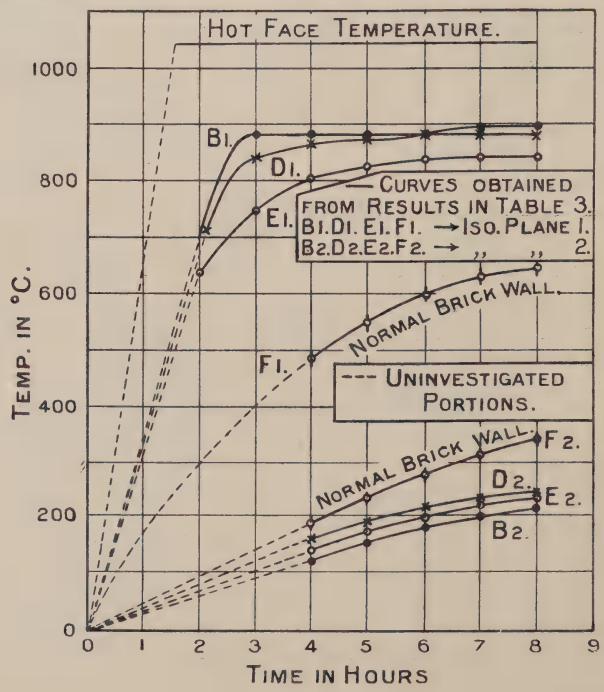

Fig. 2.

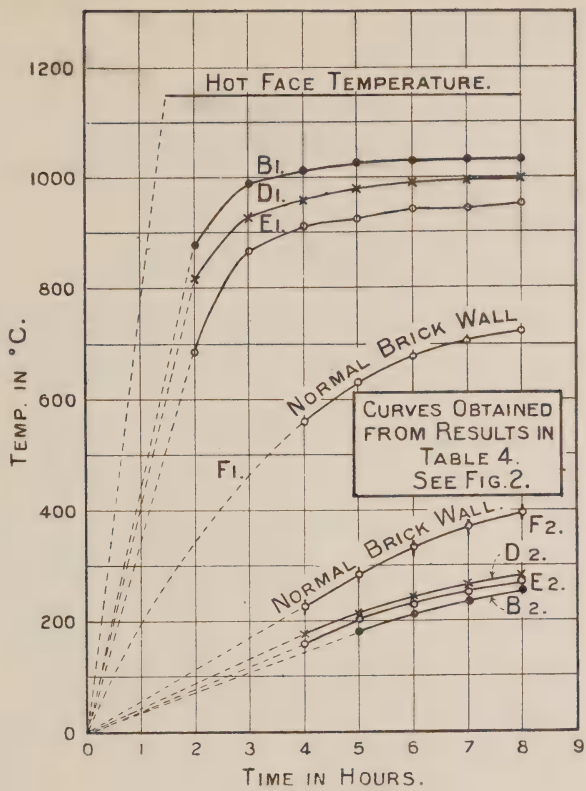

Fig. 3.

Under the heading of F (Table 8) is included the amount of heat passing through the isothermal plane I in the normal brick. Such figures are based on approximations of the equilibrium temperature of this plane, the selected values of this equilibrium temperature being obtained after a consideration of the results for material F in Tables 3, 4 and 5.

A glance at Table 8 shows the order of the insulating capacities of the materials as (1) B, (2) A and C, (4) D and (5) E. A more quantitative definition of this order is given in Table 9, which is obtained directly from Table 8, an average of the three values given for each material of this latter table being taken as the basis of the further calculation.

TABLE 9.

Percentage amount of Heat Saved by the Use of the Various Insulating Materials.				
Material B.	Material A.	Material C.	Material D.	Material E.
64·5	60·6	60·4	54·8	43·0

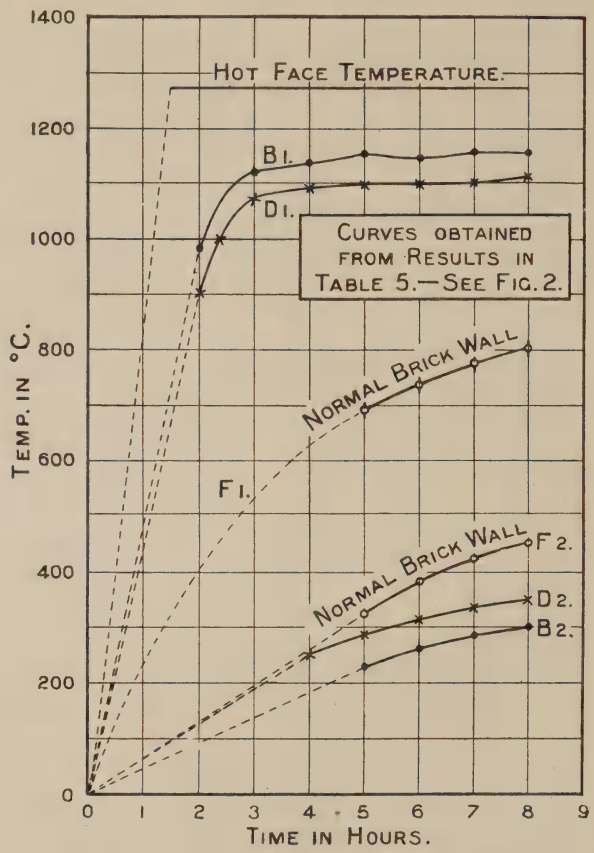

Fig. 4.

A comparison of the results for the three materials A, B and C is interesting since it seems to indicate that there is a definite porosity (apparent specific gravity, consistency or packing density) for materials of the same constitution, which gives a maximum insulating efficiency. The above results show that pure diatomaceous earth packed so as to possess an apparent specific gravity of 0·34 has a greater insulating effect than (1) the same material loosely packed (app. sp. gr. 0·08), and (2) the same material in slab form possessing an apparent specific gravity of 0·46. Petavel[4], who investigated the insulating capacity of slag wool at various consistencies, noted a similar phenomenon. He showed that the greatest insulating efficiency of slag wool is obtained with a packing of 10 lb. per cubic foot (app. sp. gr. 0·16) in low temperature practice. Boeck[5], although giving no experimental data to uphold his opinion, states that the most efficient packing for pure diatomaceous earth "flour" is 15 lb. per cubic foot (an app. sp. gr. of 0·24).

If an assumption of the equilibrium temperature of isothermal plane II be made, the approximate values of the coefficient of thermal conductivity, at a temperature of 600°C. for the several insulating materials used, can be obtained. Such approximate values are contained in Table 10.

TABLE 10.

Temperature	Thermal Conductivity in C.G.S. units, of materials.				
	Material A.	Material B.	Material C.	Material D	Material E.
600°C.	0·00278	0·000246	0·000272	0·000341	0·000460

The values for A, B and C agree well with those reported by Nusselt[6] for pure, loose kieselguhr. He reports that the thermal conductivity of this material is 0·000219 at 400°C. The value for material D is in accord with that reported by one of the present authors[1], for a fired diatomaceous earth brick, viz., 0·000350 at 600°C. Nusselt, also, gives 0·000333 as the conductivity at 400°C. of baked kieselguhr. The values for A, B and C also agree with those reported by Boeck for Sil-O-Cel "flour." Griffiths working with slag wool packed to an apparent specific gravity of 0·24 found the thermal conductivity of such a material to be 0·000342 at 476°C. However, the conductivity of slag wool can and does vary considerably by reason of the variations which occur in its manufacture.

SUMMARY.

1. The effect of various insulating materials on the temperature gradients in a firebrick wall, with three different face temperatures have been investigated.
2. From the data so obtained the insulating efficiencies of these materials have been computed.
3. Other properties bearing on the use of these materials in high temperature constructions have been noted.

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XX.—The Heat Insulation of Kilns and other High-Temperature Installations.*

By A. T. Green.

Introduction.

CONSIDERABLE progress in the methods and devices used for increasing the efficiency of the firing of ceramic wares has been made. This increase in efficiency chiefly resolves itself into four advantages, viz. : (1) a reduction in the fuel consumption ; (2) an increase in the output of satisfactory goods ; (3) an improvement in the quality of the product ; (4) an improvement in the control of firing. Some methods combine all these advantages to varying degrees. The use of regenerative and recuperative methods has been responsible for much of this progress ; a fact, which is well illustrated by the vogue of the continuous chamber kiln and the modern tunnel oven.

Another feature of this economy and efficiency campaign, which is now receiving increasing attention is the prevention of undue heat loss by way of the kiln walls and crown. A number of instances have been reported, in which the heat lost in this manner varies between 15% and 50% of the total fuel used[1]. In fact, Harrop[2] after a study of a certain continuous tunnel kiln, gave 45% of the total fuel fired as the heat loss through the walls. In many cases 60%-70%[1] of this waste can be prevented.

However, there are a number of cases where the rigid application of preventative measures would seriously affect the nature of operation. In fact, no methods of heat conservation should be superimposed on any existing heating system without a thorough definition of the desired conditions.

Heat Lost by way of the Walls and Crown.

Heat is transferred from the flames and hot gases in the kilns to the goods and to the wall and crown. Some of the heat from the walls and crown is radiated to the contents of the kiln, while a large quantity passes by conduction through the walls and from the surface by radiation and convection, to the atmosphere. The governing factors in this heat loss are, then, (1) the heat capacity of the wall, which factor, of course, includes the amount of material forming the construction ; (2) the rate of heat passage through the wall, the guiding factor of which is the coefficient of thermal conductivity of the material, composing the wall ; and (3) the radiation and convection from the surface.

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* This paper is the outcome of work done for the British Refractories Research Association.

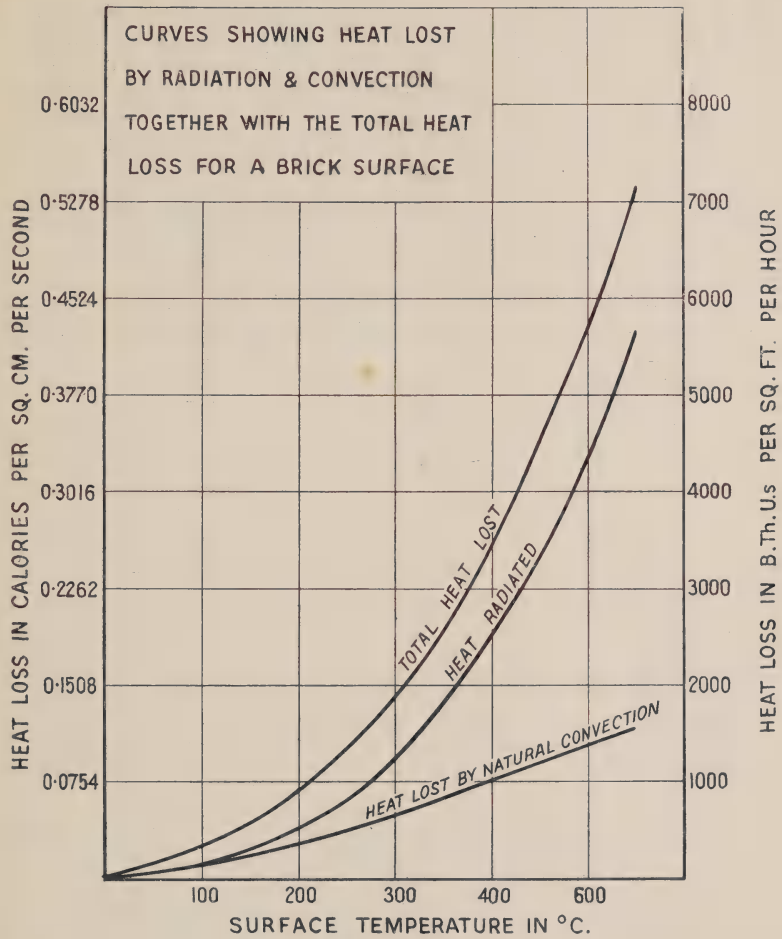


Fig. 1.

Dealing with surface losses, reference is made to Fig. 1, which shows the variation with temperature of the heat losses by radiation and convection and of the total heat loss, thus giving a quantitative idea of the surface losses. The calculation of the radiation losses is based on the "fourth-power" law, the emissivity value used being 0·72. This value has been obtained by the present author, as an average value for this "constant" between 200° and 500° for a certain firebrick surface.

The convective losses are computed from the formula used for natural convection, namely, $H = 0{\cdot}000047\ \theta^{\frac{5}{4}}$ where H is the heat

lost by convection per sq. c.c. of surface per second and θ is the difference in temperature between the surface and the atmosphere, the temperature of the latter being taken as 30°C. These convective losses would be considerably greater in an unprotected atmosphere, *i.e.*, where draughts abound. Further, they refer to vertical surfaces, *i.e.*, walls; and would be much increased when considering horizontal surfaces, *i.e.*, crowns. All this points to the fact that the convection and the total heat curves represent a minimum valuation of the heat losses. A study of these curves forms sufficient indication of the very great amount of heat that can be wasted in this manner.

Firebricks and silica bricks may be placed in the category of "medium-to-low" conductors of heat[4] (*vide* Fig. 2), which fact

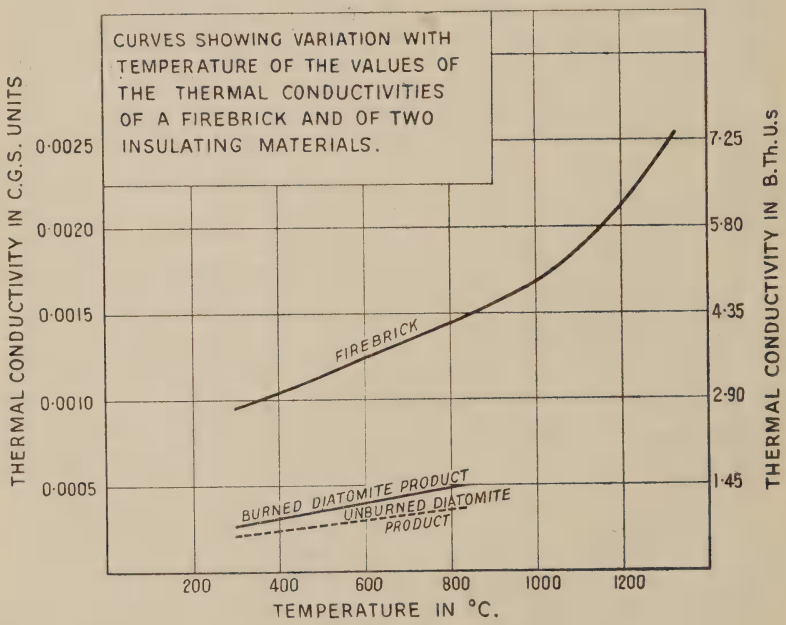
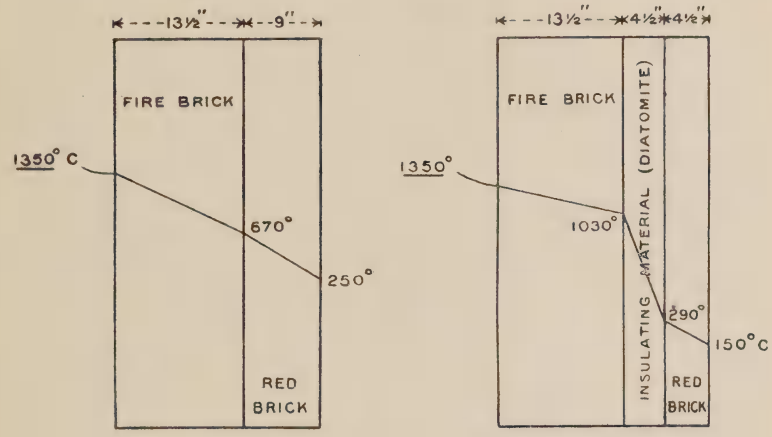


Fig. 2.

indicates that by increasing the thickness of the wall, the heat loss through the structure will be reduced. An examination of the curves *A*, *B*, *C* and *D* of Fig. 4 (this figure together with Fig. 5 is based on a similar one reported by J. H. Kruson[5] and used in the insulating work of the Celite Corporation) will show how far this increase in thickness reduces the heat loss. Thus, we find that with 27″ of brickwork the heat loss is 580 B.Th.U's per sq. ft. per hour, whereas with a wall 54″ in thickness the heat loss is 330 similar units. But, from many considerations, chiefly including the effective utilization of floor-space, it is obviously a weakness in design

to have kiln walls of great thickness, in fact, the trend of modern furnace construction is, as far as possible, to use thinner walls. Thus, it seems that, in the interests of fuel economy and of furnace design, some "buffer" material placed *in* the wall is necessary to prevent the escape of heat.

The specific heat of fireclay bricks is high, ranging from 0·193 at ordinary temperatures to 0·33[6] (approximately) at 1,250°C. Calculations based on these data show that to raise the temperature of a construction *i.e.*, kiln or furnace built up of 100,000 bricks to an average temperature of 500°C. would require a minimum of 7 tons of coal. Figures such as these, give a clear impression of the heat in a kiln structure during firing, and further indicate one of the effects of increasing the thickness of kiln walls.



FIGURES ILLUSTRATING THE EFFECT OF INSULATING MATERIAL (DIATOMITE) ON THE TEMPERATURE GRADIENT THROUGH A KILN WALL:

Fig. 3.

In general, insulating material is placed between the exterior common brick casing and the interior firebrick lining of the kiln, furnace, or oven, as a means of reducing the heat loss by way of the walls. In the case of the crown, the insulating material covers the roof bricks and is itself protected by some covering. Since by following such a plan the kiln wall can be considerably reduced in thickness the heat capacity, *i.e.*, the fuel necessary to heat the construction during firing is considerably less. Theoretically, for the greatest fuel economy, the insulating material should be the only material of construction. Such a state of affairs being impossible, a compromise based on a consideration of (1) the minimum thickness of firebrick lining necessary to give complete

structural stability; (2) the maximum temperature of working, which the insulating material will withstand, without losing its properties, is necessary. Such principles are discussed later in the paper.

Insulating Materials for High Temperature Work.

Although there are a great number of insulating materials and compositions on the market, the excessive demands of high temperature insulation can only be satisfied by a few, chiefly including slag wool and diatomaceous earth products. Slag wool has a very limited application for high temperature work, some of which limitations are indicated in the text, while diatomaceous earth products compromise the best properties of a high temperature insulator to the greatest advantage.

Diatomaceous earth, which is also called diatomite, kieselguhr and infusorial earth, is a very light porous material, principally consisting of the silicious remains of minute organisms. The deposits of this material, of which there are many good accounts,[7] are widely distributed in nature. Although diatomaceous earth is essentially a pure form of silica, the composition of the deposits varies considerably, a fact which causes much concern to the manufacturers of this variety of insulating material, since it makes the production of a standard product very difficult. The chief impurities are lime, iron oxide and clay,[8] and of these, the first two particularly, considerably impair the efficiency of the material in practice. There are a few deposits of exceptionally pure material, the best known one (which forms the basis of the Celite products)[9] being in California.

Diatomaceous earth products take a variety of forms, depending in the main, on the use to which they will be placed. The principal commercial varieties are (1) powder (unfired); (2) unfired slabs cut from the original deposit; (3) bricks, the chief constituent of which is powdered diatomite fired to 800°C. or so; (4) insulating concrete; (5) an insulating mortar. These products are all specially adapted for ceramic kiln insulation, although the insulating brick and the powder or "flour" are of widest application.

As will be appreciated by later remarks it is often essential to sacrifice some insulating efficiency for an improved structural strength. To this end it is advisable to use the fired product No. 3. One manufacturer adds about 15% of specially selected sawdust and 10% of clay to the original diatomaceous earth. He lays stress on the careful measuring of these ingredients, which are then mixed, first dry and then wet, in a double shafted mixer. The bricks are moulded in the usual slop fashion. After drying in a tunnel dryer, the bricks have to be burned off very carefully and slowly at a temperature of 800°C. The sawdust, which, of course, burns out, is added to maintain the porosity of the product, while the clay gives working and binding qualities.

An insulating material, whose original ingredients are clay and sawdust, is manufactured.[10] This product is burned at low temperatures and has a percentage porosity ranging from 45% to 50%. Underburned clay products have a much lower conductivity than the well burned material[11] and, consequently, such an insulating material has a comparatively low conductivity. However, as far as insulating efficiency is concerned it cannot be placed in the same category as a diatomite product

The Essential Properties of Insulating Materials for High Temperature Work.

The Thermal Conductivity and Porosity of Insulating Materials.

As previously defined, the action of an insulating material is essentially one of preventing heat flow through a solid structure and, of a consequence, the all-important property needing complete definition is the coefficient of thermal conductivity of the material. The value of this coefficient varies with different materials, but for successful working a range from 0·00025 to 0·00050 at 400°C. forms a satisfactory guide. Such a value is one-third to one-fifth that obtained for various firebricks in investigations carried out by the author. In specifying the coefficient of thermal conductivity of an insulating material for high temperature work, it is a careless practice merely to report just a figure for this "constant." Data at a temperature or preferably over a range of temperature, say, between 300° and 700°C. should be given.

The great insulating properties of such materials are due to the nature and quantity of the pore spaces. In fact, the structure can be conveniently regarded as an air space divided into an infinity of air cells by a minimum of solid matter. Physical reasoning indicates that the heat transmission by radiation and convection across such an air space is considerably lessened in consequence of this peculiar structure. Indeed, at low temperatures and with a maximum of pore spaces of minute size, the transmission of heat by way of these pores may approximate to an air conduction. However, the size and disposition of the pores appears to have a considerable influence on the heat conductivity of the material. Thus, some of the author's recent work[13] has shown that there is a certain packing density (*i.e.*, apparent specific gravity) which gives that greatest insulating efficiency in the use of powdered diatomaceous earth. Below this density, although the porosity is notably higher, the insulating efficiency is not so pronounced. Further, slag wool with a porosity of 88% is not so good an insulator at temperatures over 450° as is diatomaceous earth brick with a porosity of 75%. In this latter instance, the nature of the porosity of the slag wool and the diatomaceous earth are essentially different, the pores in the latter material being much more minute and disconnected.

Calvert and Caldwell[14], in a recent investigation concerning the insulating properties of diatomite have arrived at a similar conclusion. Thus, it must be concluded that so far as insulating properties are concerned, the effectiveness of an insulating material, particularly one to be used in high temperature work, depends upon the minuteness, quantity, and even distribution of the air cells, for the conductivity of air is extremely low, being of the order 0·000058 C.G.S. units at 55°C. At present there is no reliable method capable of indicating the size and disposition of the pores in a refractory material or insulating brick. Consequently, as far as the pore spaces are concerned, the best available guide is a measurement of the apparent porosity and a visual examination. The range of apparent porosity allowable is between 65%-85% although the values given for most good insulators varies between 70% and 80%. Some years ago, it was thought that an air space 2″ or so in thickness, intermediate in the wall structure, would reduce heat loss by way of the wall. Of course, the idea was based on a knowledge of the low conductivity of air. However, at medium temperatures, the rate of heat transfer by convection and radiation is very pronounced, and actually the transmission of heat is much greater than would have been the case had the wall been continuous. Ray and Kreisinger,[15] in a very efficient investigation, have indicated the fallacy of the air space.

Mechanical Strength.

In the insulation of walls of furnaces, insulating bricks are usually used. To use tamped powdered diatomite is not altogether a good practice owing to the fact that after continued working the compressed powder contracts considerably and, in certain circumstances, sags. Slag wool, which is a fibrous material and which is packed into hollow spaces between walls is particularly prone to "sagging," and when the temperature is excessive, fusion may take place. The following illustration may here be given. Slag wool was used in certain portions of a gas retort setting. It was packed into hollow spaces between the walls but gradually sagged down to form a compact mass at the bottom. In addition, the gases quickly leaked through the comparatively thin walls bounding this space, causing the space to become a flue instead of a closed pocket. Thus the loss of heat was much greater than if a solid wall of firebrick had been built. In part, this sagging was due to a change in the nature of the slag wool, a phenomenon which cannot be expected with diatomaceous earth powder. Nevertheless, laboratory experiments show that there is a defined contraction experienced with tamped natural diatomaceous earth. Such a contraction will result in the formation of air spaces of such a size as to affect considerably the insulating efficiency of the compressd powder. When insulating the crown or roof of a kiln or furnace tamped powder can be used very efficiently provided that

pressure is applied to this powder after each of the first three or four firings following its application.

In the tamping of a powder, great care is essential, otherwise some of the effects of pressure are lost. This fact springs from the peculiar features in connection with the compressibility of powders, *i.e.*, the distribution of stress in such a system.[16] It has been proved conclusively by a number of investigators that, if pressure is applied to too great a thickness of powder, the bottom layers receive none of the effects of this pressure, the apparent density of these layers remaining constant. Such results in the tamping of diatomaceous earth may give rise to uninsulated spaces in a tamped wall, which is in no way desirable, either from the point of view of insulating or structural efficiency.

A tamped wall should be built in layers of a few inches at a time. It can be mentioned here that untamped "flour" weighs between 5 and 7 lbs. per cubic foot ; the apparent density having the highest insulating efficiency is about 16 lbs. per cubic foot with the purer material, while the greatest density which can be obtained by the ordinary methods of tamping with pure diatomaceous flour is between 28 lbs. per cubic foot. A pure diatomaceous brick has an apparent density between 25-32 lbs. per cubic foot. Fired insulating bricks, in which a little clay has been added as a bond and to increase the mechanical strength, are somewhat heavier and may weigh anything up to 50 lbs. per cubic foot.

Insulating bricks are normally used for walls, and they must be regarded, at least from certain aspects, as structural units. Of course, the use of these bricks is such that they bear little or no weight of the structure, other than the weight of superincumbent layers of similar material. For such a purpose the usual range of crushing strength, from 250-400 lbs. per sq. in. is easily sufficient. In the author's work an average of about 320 lbs. per sq. inch for a variety of insulating bricks has been obtained. However, by reason of the expansions and contractions of the kiln walls considerable strains are exerted on the insulation wall. These are the strains which are liable to cause great damage to the insulation system. From the nature of the product, *i.e.*, the high porosity which must be maintained in manufacture, a much greater crushing strength than 400 lbs. per sq. ft. cannot be anticipated. To obtain a greater mechanical strength it would be necessary to induce considerable vitrification during the firing of the product. This would impair the nature and extent of the porosity, and, in consequence would ruin the insulating properties. Thus, in many instances, it is very necessary to compromise between insulating properties and mechanical strength.

Loss of Structure and its consequences.

Pure diatomaceous earth has a very high refractoriness, and

further, maintains its porosity at temperatures in the neighbourhood of 1,250°C. However, many inferior qualities of this earth, because of their cheapness, have found a way into industry. In some instances, there is no particular disadvantage in the use of this cheap product, but where the temperature of working is high, serious consequences may accrue. Because of the very fine state of division of the silica of the earth itself the presence of such impurities such as lime, iron oxide and clay leads to easy vitrification with a consequent high shrinkage and great decrease in the insulating properties. The limit of temperature to which such a material is likely to be exposed should be accurately known before building it into any plant. Then again, the temperature at which the material first begins to lose its structure must be accurately defined. In the case of insulating bricks, this knowledge can be obtained by subjecting pieces to various heat treatments, measuring any change in porosity and noting any changes, shown by visual examination. In the case of powders and slag wool, visual examination and the measurement of changes in the true specific gravity after heat treatment are sufficient to indicate any change in structure. Thus, with a sample of slag wool the author noted that the material began to disintegrate and form a powder—maybe, a physico-chemical change—at a temperature of approximately 700°C.[13] This defines the fact that it is unsafe to use this material where the temperature in contact with the slag wool is likely to exceed 700°C. With a certain variety of diatomaceous earth brick containing 5 per cent. of lime it was found that a decrease in porosity was obtained by heat treatment at 1,050°C.[13] Hence, it was concluded that it was unsafe to specify this material for temperatures over 1,000°C. Certain varieties of diatomaceous bricks are unfired, being cut out as slabs from the original deposit. These slabs show a lamellar appearance, a fact of particular significance. In experiments when heat was applied to one face of the material, the laminations of which were perpendicular to the direction of heat flow, splitting occurred along three or four such lameller planes.[13] The production of this splitting affects, to some degree, the insulating property and also the mechanical strength of the slab. This rather emphasizes the fact that it is advantageous to use a "burned" product in many phases of industrial work.

Different deposits of impure diatomite vary considerably in composition, with the consequence that, a manufacturer of insulating bricks may have serious complaints from users of his products. If, as the result of tests, on one type of material a certain limiting temperature of use is evolved, such a temperature cannot be taken as a criterion for bricks made from another batch of material. Where the highest resistance to shrinkage and loss of structure are required, *i.e.*, where the temperature of working is likely to be very high, a "shrunk" material containing at least 94 per cent. of SiO_2 and less than 1·5 per cent. of lime is necessary.

Other Properties.

Insulating material may, in the course of its service, be subjected to the influence of moisture and chemically-active gases. It is essential that such agencies do not alter the physical structure or the chemical identity of the material. In kiln firing where sulphurous gases may likely come in contact with the insulation, an inert material must be employed. From this point of view diatomite must have preference to slag wool, since this latter may be considerably altered by the action of sulphurous and other gases over continued periods.

The inherent lightness of insulating material gives distinct advantages in the rapid laying of the bricks.

THE EFFECT OF INSULATION ON THE REFRACTORY WALL.

This phase of the subject is of outstanding importance and lack of recognition of this fact on the part of many interested in the insulation of kilns has lead to much misunderstanding and failure.

In the normal passage of heat through the uninsulated kiln wall the temperature gradient is steep, and of a consequence, only a small thickness, an inch or so, is at a temperature of over 1,000°C. Cousequently, in this instance, the combined action of temperature and pressure is not one of much moment. In the case of an insulated wall (*vide* Fig. 3), maybe 13½ inches or so are over this temperature. A. J. Dale[17] in his recent study of the effect of load and temperature on the stability of fireclay refractories has indicated that the safe range for certain fireclay products is not so high as was previously imagined (*i.e.*, as judged by the refractory—under-load test devised by Mellor and Moore), and that a subsidence can take place at temperatures over, say, 1,100°C. Such considerations make it necessary to use the highest grade refractories for the insulated kiln walls, otherwise failures due to an incipient vitrification and consequent lack of stability of the fireclay may take place. It has been recorded, however, in some instances, that the fireclay bricks used in conjunction with insulating material have actually been improved in quality. It may be that a reasonably good fireclay product would develop under the influence of continued high temperatures a very pronounced "sillimanitic" structure, giving a product of superior properties to the original material forming the wall. In fact, with fireclay products, which satisfy the load-bearing limitations at high temperature, a definite improvement in the properties may be reasouably anticipated. However, against this suggestion, it is recorded that some investigators adhere strongly to the view that recrystallization, *i.e.*, the formation of definite crystalline silicates during use, gives rise to a brittleness in the product, with consequent lack of mechanical stability. It may be that this brittleness is more the result of incipient spalling due to thermal strains.

In many intermittent and other systems of heating the un-

insulated refractories are subjected to decided fluctuations of temperature. Such fluctuations are the immediate cause of the spalling of these refractories. With an insulated wall these fluctuations are rendered much less pronounced and those spalling troubles due essentially to thermal effects are mitigated to some extent.

POINTS ARISING IN THE INSULATION OF CERAMIC KILNS.

Figs. 4 and 5 show at a glance the heat saving that can be effected by the use of a layer of insulation either on the crown or round the walls. The fuel saving by such means may be anything from 10 per cent to 30 per cent. of the total fuel fired and for the

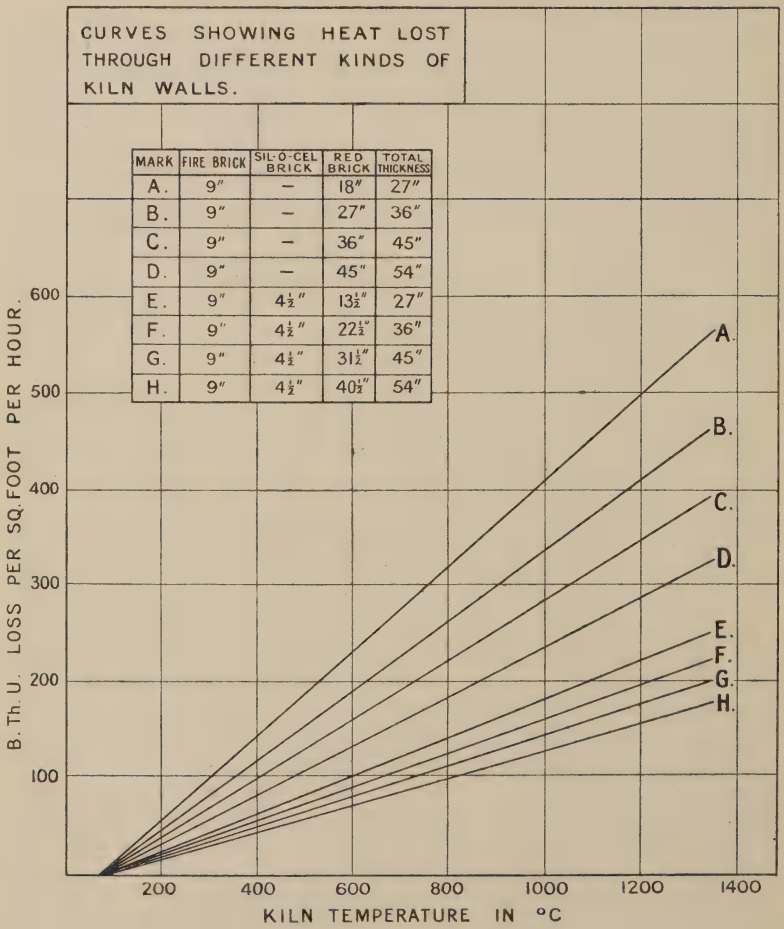


Fig. 4.

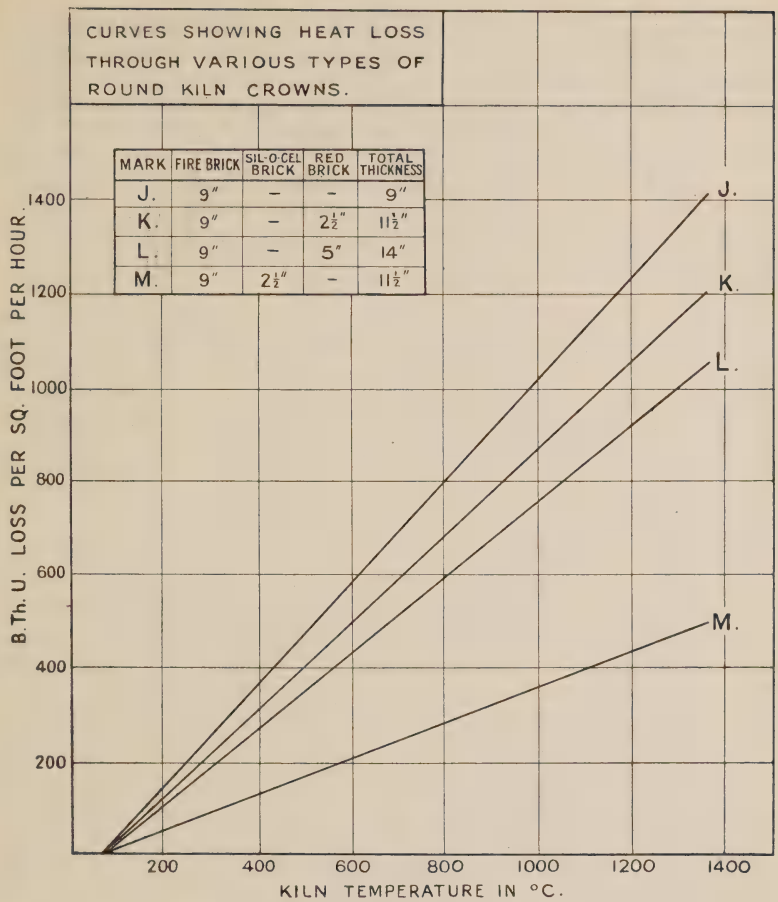


Fig. 5.

crown alone a conservation of 7–15 per cent. can result. This, however, is not the only advantage. Since the escape of heat is prevented, it is maintained in the kiln and causes a much more even distribution of the heat inside the kiln. Thus, in the ordinary round down-draught oven the great difference in temperature, which usually exists between the top and the bottom is, to some degree, eliminated in the insulated kiln, and of a consequence, the quality of the ware is much improved. A more even distribution of temperature prevents much of the practice of forcing the fires to bring the cooler parts up to the desired temperature. Again, from a similar reasoning it follows that the firing of the ware in the down-draught kiln can be completed in a shorter time, if necessary. Given the use of the best type of refractories in

the kiln construction, particularly in the crown, and a careful design of the crown itself, there can be no doubt that insulation is a positive help towards economy. There is, however, one possible serious disadvantage to the ordinary manufacturer of refractories and other ceramic wares, as far as the down-draught kiln is concerned. In some instances, which have come to the author's notice, an attempt has been made to insulate an existing kiln, with little alteration of design, *i.e.*, thickness of walls and such like matters. The result has been that in the intermittent systems, where the rate of cooling must be necessarily rapid to admit of economical working, that the escape of heat has been impeded and the duration of the process considerably increased. Obviously, then, a greater loss from wasted time than from wasted fuel accrues. It seems then that where the walls of a working kiln are particularly thick it is not advisable to insulate the existing walls. However, the crown may be insulated and a compromise so effected. Similar reasoning applies to a continuous chamber kiln although by increasing the number of chambers the full effect of insulation may be realized. This however greatly increases the initial capital cost of the installation and the floor space used.

The thickness of the walls of a kiln is a very interesting problem. Walls of great thickness are in common use, since, by so increasing this dimension a certain proportion of the loss by way of the walls is prevented. This, of course, follows from the fact that, the surface temperature of the outside wall and the heat loss by radiation and convection are reduced by increasing the thickness. However, this great mass of brickwork acts as a great reservoir of heat, which is wasted, and further, which increases the duration of the cooling period. The use of insulating material allows the use of a much thinner wall, *i.e.*, a wall of refractory as thin as is compatible with the necessary structural strength. The conception of this structural strength must be based on a knowledge of the effect of temperatures of 1,000° or over on the properties of refractories, since the insulation will maintain such a conditioning factor. Walls $13\frac{1}{2}''$–$18''$ thick made of superior refractory material followed by $4\frac{1}{2}''$ insulation and $4''$ to $8''$ of common brick appear to satisfy the main conditions. The success of a wall of less thickness than the above dimensions appears to be too much a matter of chance when high temperatures of firing, *i.e.*, for the burning of refractories, are the rule. Such a wall will be about half as thick as some. The heat capacity will be much less than the thick uninsulated variety and, consequently, it cannot be expected that there will be a tremendous difference in the duration of the cooling. Nevertheless, calculation indicates that the insulated wall will take somewhat longer to cool. This may be partially compromised by a more rapid rate of heating.

Insulating bricks are almost invariably used in wall constructions, and it is in every way advisable that these bricks are of the fired

variety as the temperatures are likely to be sufficient to cause a splitting of the material along the original laminations of the deposit. An insulating mortar supplied by the manufacturer of the products is supplied with the bricks. Because of their light weight there is no particular difficulty in laying these bricks, a job which takes a comparatively short interval of time. Again, in the design of the insulated wall a great conservation in material and labour results owing to the great reduction in dimension.

The life of a down-draught kiln depends in great measure on the success or failure of the crown. Trouble with the crown is often accentuated by the use of insulation owing to the very high temperatures resulting in the crown bricks giving rise to volume changes of a peculiar order. In fact, much prejudice concerning insulation rests on the reported failures of insulated crowns. The design and material of construction of this part of the kiln must receive the highest consideration. Kruson[5], in his valuable article, states that the height of the crown from the spring line to the top inside should be approximately one-fourth the diameter of the kiln and that the banding of the crown seat should be carefully considered and carried out. A refractory which shows the best qualities under the more recent load testing devices, *i.e.*, the measurement of the subsidence taking place at a temperature in the neighbourhood of say 1,300°C. is essential if freedom from failure is to be assured. With due regard to these factors, there is no reason why the greatest efficiency from crown insulation should not be obtained.

Either bricks or the powder give good results for insulating the crown, which, of itself, is about 9″ in thickness. Possibly, the powder is more generally used. This material can be applied to any old kiln or—after the first fire owing to the settling of the crown—to a new one. The powder is made in the form of a paste with water and is worked over the crown first to a thickness of about 2″. After another firing or so another layer of a similar thickness is worked. The whole of this is eventually covered first by a layer of 1″ firebrick splits and then by some water-proofing material, usually of a bitumastic nature. Because of the great reduction in the surface temperature of the crown after insulation, water-proofing materials of this nature can be used. Such a construction —between 4″ and 5″ of insulating powder—is sufficient for all practical purposes.

The tunnel kiln, the use of which has made such rapid progress during the past decade, forms an ideal plant for the use of insulation. After due regard has been paid to the quality and thickness of the refractory lining, insulation can be applied without considering many of the qualifications which apply to the down-draught kiln. By such practice an even temperature gradient is maintained throughout the length of the kiln, the walls since they are protected from the formation of hot patches and uneven gradients by the insulation, in the main, are reported to improve with duration

of working. The design of a tunnel kiln does not warrant very thick walls and the use of insulating material is of extreme help in this connection.

The cost of insulating a kiln depends primarily upon the material used and the extent to which such conservation of heat is possible. Since the quality of the material to be used is dependent on the temperature it will be required to withstand, very high temperature installations should use the purer forms of diatomite products. Using the most expensive products, the fuel conservation is such that the initial outlay is retrieved in a few months, provided, of course, that no drastic structural alterations are necessary before the insulation can be completed.

NOTES ON THE APPLICATION OF INSULATING MATERIAL TO OTHER HIGH TEMPERATURE INSTALLATIONS.

There are few branches of high temperature work in which insulation cannot be usefully applied in one form or another. In fact, there are few applications which possess the same inherent difficulties as those concerning the ceramic industry.

Insulating methods find great encouragement in the iron and steel industries where fuel economy is always studied in its widest aspects. In illustration it may be mentioned that the blast stoves and many reheating and heat treatment furnaces, producers, etc., are now suitably insulated in modern iron and steel plants. In the gas industry the value of insulation is being keenly recognized, a fact which may have a two-fold origin, *e.g.*, the comfort of the workers in vertical retort plants and the desire for fuel economy. The first reason has been instrumental in causing the effective insulation of the tops of the setting by a layer of insulating bricks. The difference in working conditions caused by such an innovation is nothing short of startling. In some works the fronts of the settings, generally where the plant is congested, are covered by a layer of insulating bricks for a similar reason. An incidental effect of this insulation must be that the temperatures round the retorts are made more uniform and that quite an appreciable conservation of heat is obtained, although this latter effect is not so pronounced as could have been the case had the insulating material found a place in the interior of the wall itself. However, many gas engineers are now placing the materials in the walls with the object of heat conservation and even temperature distribution. The recovery of waste heat from gas installations has received considerable attention of late, and there can be little doubt that adequate insulation has played a big part in the success of certain plants set down for this recovery. J. S. Thorman[18] in a recent paper to the Southern Association of Gas Engineers and Managers has shown in a conclusive manner how insulation succeeds in making his waste heat boiler system a very efficient unit. In the course of his remarks he stated that "observations were made with the

object of determining what would be the loss of waste heat due to radiation from the firebrick lined steel connecting mains between the base of the chimney shafts at the outlet of the vertical settings and the inlet to the waste heat boilers. Readings of the temperature of the waste gases at the base of the chimney shaft and further readings 24 feet higher up were taken, and it was found that there was a temperature drop in the waste gases passing over this area of 200° C. between these two points. This loss of heat to the waste gases exposed to a surface of firebrick lined steel shaft, equivalent to the surface to which the gases would be exposed between the base of the shaft and the waste heat boilers, was a serious one, which would reduce the estimated steam production from 1,300 lbs. to 975 lbs. per hour per setting."

From this knowledge it becomes obvious that some type of insulation must be used in the firebrick lined steel collecting mains. After a number of experiments of a very practical nature on a number of insulating materials and compositions, the conclusion was drawn that a 3″ firebrick lining in contact with the gases, and 3″ of insulating brick made from diatomaceous earth, between this firebrick and the exterior steel shell was the most efficient. In the type of installation referred to by J. S. Thorman, this encasement is now a matter of "practical politics," and by its use the heat losses between the base of the shafts and the inlet to the boilers have been reduced from 25 per cent. without insulation to 6 per cent. with insulation—a very effective saving.

Conclusion.

It is obvious from the foregoing remarks that the selection of insulating material for high temperature work cannot be based on insulating efficiency alone. Before selecting such a material it is absolutely essential to have a complete knowledge of the circumstances of its future use, particularly regarding the face temperature, to which it will be subjected. The following data will then serve well in the selection: (*a*) The coefficient of thermal conductivity at temperature between 300° and 800°C.; or the insulating efficiency[13] based on a test simulating industrial conditions; (*b*) Percentage porosity, together with some description of the nature of the pore-spaces; (*c*) Refractoriness (*i.e.*, Specification test), together with the temperature at which the material disintegrates or otherwise loses its structure; (*d*) Crushing strength as an indication of the mechanical strength.

Finally, the author wishes to thank the Derbyshire Silica-Firebrick Co. for their interest and help in the work on insulation, and the Celite Products Co., whose book on "Heat Insulation" has been a great assistance in supplementing, laboratory and technical observations made by the author.

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DISCUSSION.

THE PRESIDENT (Mr. F. WEST):—The thing that interests us is getting down to more detail and to find an insulating material at as reasonable a cost as possible. I have found great difficulty in using insulating materials, in connection with kilns, I doubt whether it is of any great advantage. As already pointed out the cooling question comes into operation. It might be advantageous in tunnel kilms but when you consider continuous chamber kilns or intermittent kilns you find that you reduce your output very much if you insulate them. I believe in insulating the tops or crowns, but as regards the sides, I do not think there is anything in it. Otherwise in places where you are keeping a constant heat on, like in retort settings, it is a great advantage to keep the heat in.

There is certainly some valuable matter here and the paper is now open for discussion.

SIR WM. JONES:—I think the paper we have listened to opens up a great field for serious consideration and indicates where enormous econony may be effected. I think our President has touched on the difficulty that has to be regarded in connection with the insulation of kilns because of the double phase aspect of kiln working. One can easily appreciate the great advantage secured in constructing kilns with the firing zone having comparatively thin walls but with effective insulation—that must, of course, be very economical; but when it comes to the reverse action of cooling the material which has been fired then the difficulty to be overcome of retaining heat, that you are anxious to dispose of, presents itself. I think this problem of insulation of kilns is one that is worth a great deal of study for the very reason that it is full of difficulties.

One of the troubles experienced in retort construction has been the great weakness of the insulating material, and its want

of resistance to compression, caused by the expansion of the structure itself during the heating up until its point of maximum firing, is reached.

One has to build kilns with ties and bracings, and if you interpose an insulating material for the purpose of conserving the heat and preventing radiation, you counteract in large measure the very use for which the buckstays and tie rods are employed.

When it comes to vertical gas retorts other considerations apply because there the main objective is to retain the heat in the retort at a constant temperature and you have not the alternating heating and cooling actions such as obtain in a kiln.

I know from experience, although insulation of vertical retorts is comparatively new, we found that the application of an efficient insulating material to the exterior of the walls of the retorts did result in something like 30% economy in regard to the fuel used in the producers coupled with the increased throughput of the retorts. That is a very important advantage.

I think it is very good that we should have this paper before us to-day. It should engage the attention of all refractory makers and kiln builders because this question of fuel economy must of necessity be a matter of the greatest interest to all who are engaged in industries where fuel consumption is a vital factor of cost of production.

Mr. Frank Russell, F.G.S.:—I should like to thank Mr. Green very sincerely for his paper as insulation is a subject to which we can very well give some attention just now. We are all complaining of bad trade anf low profits whilst a good deal of the latter may be going into the air, and we may be able to save money by saving coal on our kilns, and thus, perhaps, make a profit where we previously made a loss.

We made an experiment by insulating one kiln with diatomite bricks and have since saved several tons of coal at every burning of this kiln.

An ordinary kiln wall is perhaps 4ft. thick, and the heat produced is first of all absorbed by this wall, which has to be soaked with heat, so that its inner lining may be of the same temperature as the goods to be burnt, until which time we cannot raise their temperature to the correct height. Some of this heat gets through to the outside and is lost by radiation, and it is necessary also to supply sufficient heat to make up for this loss, as the temperature cannot otherwise be maintained. Here are two avenues of regular loss.

If you put an insulating partition vertically in the kiln walls, nine inches from the inner wall, you have only to soak nine inches of wall instead of four feet and practically none of the heat escapes to the open air to be lost by radiation. There is thus a saving in the consumption of coal because less is needed to reach

and maintain a given temperature.

Dr. Mellor has mentioned that a bogey may arise with regard to the possible length of time occupied by the cooling period, but we have not found much difference, if any, in this respect since the insulation. I should like to point out that most of the cooling of a silica brick kiln at any rate, takes place through the flues from the inside, and as there is only nine inches of wall to cool in an insulated kiln, instead of four feet, and all this nine inches is on the inside, the cooling of an insulated kiln may easily take even less time than that of an ordinary kiln.

Mr. H. J. Toogood:—As a designer of vertical retort settings, I have used insulation materials since 1909. Since 1918, when the porous insulating bricks became a practical commodity, these porous bricks have been extensively used by us, nearly always on the outer surface of the setting walls.

I understood Mr. Green to say that Porous Bricks begin to lose their properties at about 1000°C.=1830°F. This being so, would it not be better to confine their application to the outer surface of the walls, where they would never attain or approach such a temperature as 1,000°C, whereby their properties would remain unimpaired at all times.

In vertical settings with these bricks applied externally, the wall's surface is so cool that, paradoxical though it may seem, the hand can be place and retained on the walls, even though the interior temperature but a few feet away may be at 1400°C= 2,550°F., which would seem to show that, not only was the comfort of the men secured, but the maximum heat conservation was obtained by this external application.

Stating this in other words, if the efficiency of insulation of the microscopic pores be at the maximum at lowest temperature, then the outside surface is the best point of application.

I have no experience of insulating kilns such as described in the paper, but it would seem to me that even here external insulation could be preferably and advantageously applied, as being light, the porous bricks could be built into frames, and placed on, when raising the heats of the kilns, and removed when cooling the kilns.

Mr. W. Boyd Mitchell:—Recently I heard from the works' manager in a steel works that in a furnace he insulated the floor and this had shown an enormous saving. I should like Mr. Green's opinion of the difficulties of insulating the foundations.

Mr. A. E. J. Vickers:—I should like to add a few remarks in extension of those made by Mr. Toogood with respect to the application of the insulating material to the outside wall of a furnace of retort setting.

My own experience, which extended for a fairly long time,

was gained in connection with a battery of horizontal retorts, some of which had the outer walls insulated with a material, which is one of the best obtainable, and which has been spoken of very favourably by Mr. Green, as a result of his experiments upon it. In those beds which were insulated, the insulating material was made to take the place of the ordinary brick facing (it is not the custom in horizontal retort practice to use such high class materials for facing beds as is the case with vertical retorts). During the operation of the plant for a period of two years the atmospheric temperature opposite the beds which were insulated was considerably higher than that opposite the beds which were *not* insulated: also it was decidedly more inconvenient to work in front of the beds which had been insulated. A possible explanation may be found in a study of Fig. 3 of Mr. Greens's paper. The effect of the outer layer of insulating material was to raise the temperature of a point represented by 670°C in his left hand diagram to something in the neighbourhood of 1,050—1,000; then, while there was a very steep gradient through the insulating brick temperature it was not sufficiently steep to bring the face of the bed to the ordinary temperature which persisted outside, but had the effect of raising this fairly considerably with the results described above. It would seem, therefore, that the only place to apply insulation material is as near to the furnace side of the furnace wall as possible without destroying the insulating material. The sandwich illustrated in the right hand diagram of Fig. 3 shows the effect of this method of insulation. It is unfortunate that insulating materials have not the strength and refractoriness necessary for their use as the furnace lining itself; the ideal insulating material would be a perfect refractory; we could then line our furnaces with it, and obtain the total reflection of all the heat generated from the walls, for use inside the furnace and none would escape at all.

There is another, and, in many ways, far more important, application of the work of my friend Mr. Green upon the subject of heat insulation. It is a well established fact that the vertical retort is by no means an unmixed blessing; while it has done much to ameliorate the work of the gas stoker, by doing away with the dust, smoke and fumes of sulphur dioxide which are a concomitant of the old fashioned horizontal retort house, it has exacted payment for its benefit by an increase in the incidence of carcinoma and sarcoma among the men who work in the upper stages of the installations. These two terrible diseases seem to be caused by the combined effect of certain of the products of the decomposition of coal by heat which are always present in the atmosphere at this point of the plant, and radiant heat of a particular wave length which is also given off by the upper portion of the setting. If this escape of radiant energy can be prevented, then

the two pathological conditions cannot develop; and it seems to me that an application of Mr. Green's results to prophylactic measures for the prevention of these two diseases would be of inestimable benefit to the workmen.

Mr. A. T. GREEN:—I wish to thank all who have helped to create interest in the paper by promoting such an able discussion. Although the subject differs somewhat from the usual technological issues of the Society, its general importance to the industry cannot be doubted.

The President (Mr. F. West) and Sir W. J. Jones make a bogey of my point concerning the increased duration of the cooling period, when the wall and crown of a kiln are insulated. It is, therefore, refreshing to find Mr. F. Russell bringing forward able argument and practical data to show that, at least with a silica brick kiln, where the more modern principles of kiln design, particularly appertaining to the reduction of the kiln wall thickness, are in vogue, the time of cooling is not materially increased. Considerable time can be saved in the actual heating of the goods in an insulated kiln owing to the fact that heat which would otherwise escape by way of the walls and crown is kept in the kiln for the production of useful work. Therefore, if some extra time is required to cool the insulated kiln, the duration of firing *i.e.*, from the setting to the drawing of the kiln, will be very little different from that obtaining with the uninsulated kiln. Again, calculations based on a comparison of the thin insulated kiln wall and the thick uninsulated wall do not show a great difference in the rate of cooling of the two structures. Even so, it is a certainty that the crown should be insulated, such a practice saving from 10–15% of the total fuel used, at a very small initial outlay.

Mr. A .E. J. Vicker's contribution to the discussion, in part, intends an answer to Mr. H. J. Toogood's question. However, I should like to point out to Mr. Toogood that, if the insulating bricks are placed on the outside, the firebrick wall then becomes soaked with heat, and acting as a reservoir takes up more heat than would be the case if the insulation were placed inside the firebrick wall. Therefore, although an exterior insulation effects some heat conservation, the interior insulation is capable of far greater heat saving. The influence of porosity in the sense suggested in Mr. Toogood's remarks, hardly comes into play because of the large temperature gradients, which must exist in the insulating medium in use. Thus, the *average* temperature of an insulating partition placed in the wall of a high temperature installation is rarely more than 600°C.

Mr. W. B. Mitchell makes mention of the insulation of furnace foundations. In metallurgical practice where the processes, such as reheating the ingots etc, are continuous, the saving of

heat by the use of an insulating concrete in the floors is a highly desirable procedure. The application of this process to ceramic kiln construction is still in the experimental stage, but, as far as the actual saving of heat is concerned, it cannot fail to bring very good results. It may be, that the insulation of the crown and the foundations, and the use of the ordinary firebrick wall will form an admirable compromise as far as the rate of cooling of the kiln is concerned.

I should like to thank my colleague Mr. A. E. J. Vickers, for his contribution, which introduces such a very important viewpoint concerning the necessity of insulation in gas works' practice.

XXI.—The Rapid Production of Vitrified Clay Wares by the Combined Effects of Heat and Pressure.

By A. J. Dale, B.Sc., A.I.C.

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INTRODUCTORY.

IN 1868, H. Tresca[1] obtained evidence that dried clay flows like a liquid under an applied pressure of 10,000 kg. per sq. cm., while W. Spring[2] in 1884, stated that purified alumina, melting normally at 2,000°C., could be melted at ordinary tem-, peratures under a pressure of 75,000 lb. per sq. in. Following a number of determinations on the refractoriness of firebricks, etc., under load conditions, J. W. Mellor[2] in 1917, put forward the suggestion that, with certain clays from which the water has been removed, pressure should be capable of performing the "work of vitrification" at ordinary temperatures.

As the result of a study of the flow of firebrick materials under stress at high temperatures, the present author was led to a somewhat similar conclusion—that the *combined effect of heat and pressure* should enable the production of a vitrified clay ware in a minimum of time (Prov. Pat. 8935/24). In view of the possible commercial application of this principle to the rapid firing of certain types of material, it should be noted that such a process would not necessarily involve the heating of the material *in situ* in a die; the powdered clay or mixture could be subjected to a preliminary heating in the powdered condition before insertion in a heated die, thus enabling water smoking, dehydration and oxidation periods to be carried through without risk and with the utmost rapidity. Should this method yield a commercially useful product, the reduction in time and labour achieved by the elimination of slop moulding, and of careful and prolonged drying and firing periods must go a considerable way towards ensuring its economic success as a large scale proposition.

THEORETICAL.

Distribution of Pressure in Columns of Powders.

It appears desirable, before presenting experimental details and results, to deal briefly with what must be one of the chief intricacies in the briquetting of powdered materials under pressure at ordinary temperature, namely, the heterogeneity of the pressure distribution throughout the pressed mass.

The distribution of a uni-directional pressure applied to contained fluids—liquids and gases—is characteristically homogeneous. In the case of solids subjected to a uni-directionally

applied pressure above a certain magnitude, the pressure distribution is obviously heterogeneous—*e.g.*, sliding-cone failures obtained in the compressive testing of certain constructional materials.

With powdered materials contained in tubes or dies and subjected to a uni-directional pressure, the pressure distribution throughout the mass is extremely complex, and herein lies the explanation of the small measure of success attending certain briquetting and dry-pressing processes[5].

Pressure applied to the upper surface of a column of powder is not transmitted uniformly throughout the length of that column. A considerable fraction of the applied pressure is taken up by the side friction between the powder and the walls of the die or container; within the powder itself a *pressure gradient* exists and there is a reduction of pressure from layer to layer as the distance from the upper surface increases.

As is to be expected, and as certain preliminary experiments by the author have indicated, there exists also a horizontal heterogeneity of pressure distribution.

The recent work of E. E. Walker[6] and of J. H. Shaxby and J. C. Evans[7] has thrown some light on the problem of powder compressibility. Thus, Walker has brought forward the following approximate equations as the result of experimental work on the effect of uni-directional compressive forces on powders contained in a cylindrical die.

$$V = C - K \log P \quad \ldots \quad (1)$$

where V = Volume ratio* of powder, P = applied load and C and K are constants.

also $$V = C' + ml \quad \ldots \quad (2)$$

where V = volume ratio of a layer of powder at depth l from surface, C' = volume ratio of layer immediately at the surface and m = a constant.

Combining equations (1) and (2) we get $K \log P = C'' - ml$

or $$dp/dl = -m.P/K \quad \ldots \quad (3)$$

a relation indicating that the rate of decrease of pressure with depth is proportional to the magnitude of the externally applied pressure.

Shaxby and Evans on the other hand deduced the following equation from theoretical considerations and demonstrated experimentally its close approximation to the truth.

$$p = \frac{d\,g\,R}{2c} + \left(P - \frac{d\,g\,R}{2c}\right) e^{-\frac{2cx}{R}}$$

where p = pressure in a section at a distance x below the surface, P = external pressure, d = density of particles, R = radius of die, and c = a gradient constant.

$$* \text{Volume Ratio} = \frac{\text{App. Vol. of Powder.}}{\text{Actual Vol. of Powder}}$$

If we regard $dgR/2c$ as small compared with P, this assumes the form

$$p = Pe^{\frac{-2cx}{R}} \quad \ldots \quad (5)$$

whence, regarding P as constant,

$$dp/dx = -2cp/R \quad \ldots \quad (6)$$

Apart from the indications of the above work as to the possibility of exercising a certain amount of control on the initial porosity of dry pressed materials, the results have a direct bearing on the problem in question..

Equation (6), which is of the same form as equation (3) obtained by Walker, indicates the rate of decrease of pressure with depth to be

(*a*) Directly proportional to the "frictional constant," c, which in its turn is proportional to μ, the coefficient of friction between the powder particles and the die walls.

(*b*) Inversely proportional to the radius of the die.

(*c*) Directly proportional to the applied pressure itself. Cohesive forces are not, however, included in the above consideration.

The Effect of Temperature on the Compression of Clays, etc., in Dies.

As has been indicated, the transmission of pressure down a column of powder is governed to a large extent by the magnitude of the friction between the powder particles and the die walls.

Furthermore, a certain amount of work on the softening and sintering of amorphous and crystalline materials has shown that surface softening takes place at a much lower temperature than the softening or melting points of the mass[8].

Consequently, since side friction is essentially a surface effect, it is to be expected that side friction can be so considerably reduced by heating to a temperature far below the normal softening or melting points, as to allow a fairly homogeneous penetration of pressure throughout the mass; in other words, there is sound theoretical justification for the assumption that the difficulties encountered in the preparation of a comparatively homogeneous and coherent product by the action of pressure on a powdered granular material at ordinary temperatures should be considerably minimised by carrying out the pressure treatment at temperatures within the surface softening range of the material.

Experimental.

Apparatus and Method of Experiment.

The load test furnace offered a form of apparatus suitable for the investigation of the combined effects of temperature and pressure on clays and other ceramic materials, but its adoption for the purpose of this work necessarily incurred certain experimental limitations which should be taken into account when the appended results are considered.

For example, without decided structural modification of the furnace, it was not found possible to force the compressed material from the die at working temperatures (*vide infra*); the mechanical stability of the double-lever system of loading restricted the maximum load value to 330 lb. per sq. in.; while the dimensions of the furnace limited the area of the die aperture to the value given later.

A special die, press-block and base plate were obtained; these were of Vikro metal—a nickel-chromium alloy*—and have withstood repeated load treatment with the exterior of the die at 1,100°C. without showing any external signs of distortion or undue corrosion.

The die aperture was $1{\cdot}8 \times 1$ in., depth 2 in., situated centrally in a cylinder of $3\frac{1}{2}$in. diameter.

The die, resting on the base-plate, was supported in the hot zone of the furnace by means of a column of carborundum blocks, the necessary pressure being transmitted to the material through a carborundum thrust rod.

As a result of indications from preliminary work, the experiments reported in this paper were carried out at a furnace temperature of 1,100°C., the material inside the die being at a temperature of approximately 1,050°C.

The clay or mixture under investigation was quickly dried and ground, the required amount poured into the die already in position in the furnace, the temperature of the furnace raised as quickly as possible to 1,100°C., and, thereafter maintained constant at that value.

As soon as the required temperature had been attained, the press-block was lowered into position by means of a nichrome wire, the thrust rod placed in position and the desired load applied.

The recording modification described in a previous report[4] made it possible to follow the compression of the materials of experiment under the combined effects of load and temperature.

Materials of Experiment.

After due consideration of the experimental limitations of the apparatus, the following materials were chosen for investigation:

(1) Calcareous earth, used for common building bricks, ordinary refractory value, Cone 4.
(2) Wetley marl, a local surface clay; ordinary refractory value, Cone 9.
(3) Cone 16 mixture.
(4) Vein quartz containing 99·5% SiO_2. Ordinary refractory value not determined but certainly greater than Cone 33.
(5) Stourbridge fireclay; ordinary refractory value, Cone 29/30.

Experimental Results.

The results which follow appear to be demonstrative of the general possibilities of this method of inducing rapid vitrification.

* Present cost, 7/6 per lb.

Any unqualified pressure values mentioned are to be regarded as the minimum pressures under which definite positive results were obtained.

(1) *Calcareous Earth.*

Effect of a definite heat treatment at ordinary pressures.

A known amount of the powdered material, dry-pressed at ordinary temperatures under a load of 216 lb. per sq. in., was heated while still in the die to a furnace temperature of 1,100°C. in one hour; the temperature was held at this value for a further period of one hour.

The cooled product could be powdered between the fingers and showed complete absence of the usual characteristics of vitrification.

Effect of a combined Heat and Pressure Treatment.

A similar amount of powdered material, after being heated in the die to a furnace temperature of 1,100°C., was subjected at this temperature to a pressure of 216 lb. per sq. in. After one hour the die was removed from the furnace, allowed to cool, and the contents forced out by means of a hydraulic press. The product possessed all the characteristics of advanced vitrification; it possessed an extremely close and uniform texture and when struck, emitted a definite metallic ring.

(2) *Wetley Marl.*

This material, dry pressed at ordinary temperatures under a pressure of 315 lb. per sq. in., and subjected to a heat treatment as above, yielded a non-vitrified product which could be easily disintegrated. The same material after heating for one hour at a furnace temperature of 1,100° under a pressure of 315 lb. per sq. in. was converted into a hard, dense, laminated, vitrified product.

(3) *Cone* 16 *Mixture.*

The extremely low degree of cohesion exhibited by this mixture, dry-pressed at room temperature under a load of 250 lb. per sq. in., was not materially improved by a one hour heating at 1,100°C. This heat treatment, however, carried out under a pressure of 250 lb. per sq. in., gave a product possessing marked cohesion and mechanical strength.

(4) *Vein Quartz.*

The sample under investigation was ground mechanically for half an hour in an iron mortar. The dry-pressed material (270 lb. per sq. in.), both without and with heat treatment (*vide supra*), showed an almost complete absence of cohesion.

After the combined heat and pressure treatment (270 lb. per sq. in.) the product possessed marked mechanical strength and cohesion and was comparable with a fine-grained sandstone.

(5) *Stourbridge Fireclay.*

Positive results were not obtained with this clay.

Before proceeding to a consideration of the general indications of these results, it is important to add that many other determinations with the above materials, carried out under pressure values lower than those given in this section, yielded either negative or inconclusive results, so far as the production of a vitrified product is concerned.

It is also significant that, in the case of certain experiments performed at lower temperatures, a casual inspection of the products afforded sufficient evidence of a heterogenity of pressure distribution, which the use of higher temperatures undoubtedly minimised and, in some cases, practically eliminated.

Summary and Conclusions.

The results reported in this paper prove conclusively that the application of comparatively low mechanical pressures can exert a considerable accelerating effect on the rate of vitrification of certain types of materials at temperatures in the region of 1,050°C. Without undue stretching of the available data, it appears probable that this acceleration will be much more marked under the higher pressure values (up to 4000 lb. per sq. in.) attainable in a number of commercial briquetting machines, which, in addition, are capable of exerting pressure simultaneously in two opposite directions. The establishment of this principle appears to open up the possibility of the rapid firing of tiles, building bricks and articles made from surface clays and other materials possessing fairly low refractory values; and of the briquetting, without bond, of certain calcined refractory oxides, *e.g.*, alumina, magnesia[9] or zirconia, which are known to exhibit the phenomenon of sintering at temperatures 1,000°C. lower than their true melting points.

Certain refractory carbides[9] and graphite[10] might also be mentioned in this connection. It is, however, the writer's opinion that, in view of the practical importance of pressure distribution which has been previously emphasised in this report, definite statements regarding the applicability of the principle to the production of larger shapes should be avoided until actual experiments can be performed using higher initial load values on materials contained in a die with dimensions of at least $9 \times 4\frac{1}{2} \times 3\frac{1}{2}$ in.

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XXII.—Further Experience with the Dorr Mill.

By A. S. W. Odelberg.

In a previous paper (Trans. **22**, 2, 1923) the Dorr Mill Plant, as arranged at Gustavsberg was described with the aid of a diagram, which is here reproduced for reference. Since reading that paper I have made the grinding perfectly automatic; by opening the tap under the thickener, the finished material is allowed to run constantly to the flint arks, the rate being regulated to about 1 litre in 15 seconds. The specific gravity is 1·6 to 1·5. It is to be borne in mind that water must be constantly admitted from the main to the classifier to replace the water going to the flint arks. This water is regulated according to the height of the water in the sump. In this way the grinding takes place quite automatically, and the work of the man supervising the grinding is reduced to that of an onlooker. A great advantage of this automatic regulation is that the circulation of the material takes place without shock or disturbance at any point or time. This is clearly shown in the thickener, where periodical cloudiness is no longer observed at the overflow.

During the past year, we have been carrying out at Gustavsberg, a series of experiments, the aim of which is to determine the best speed at which to drive the mill, and the comparative output per electric unit as compared with a large batch grinding cylinder of the usual type.

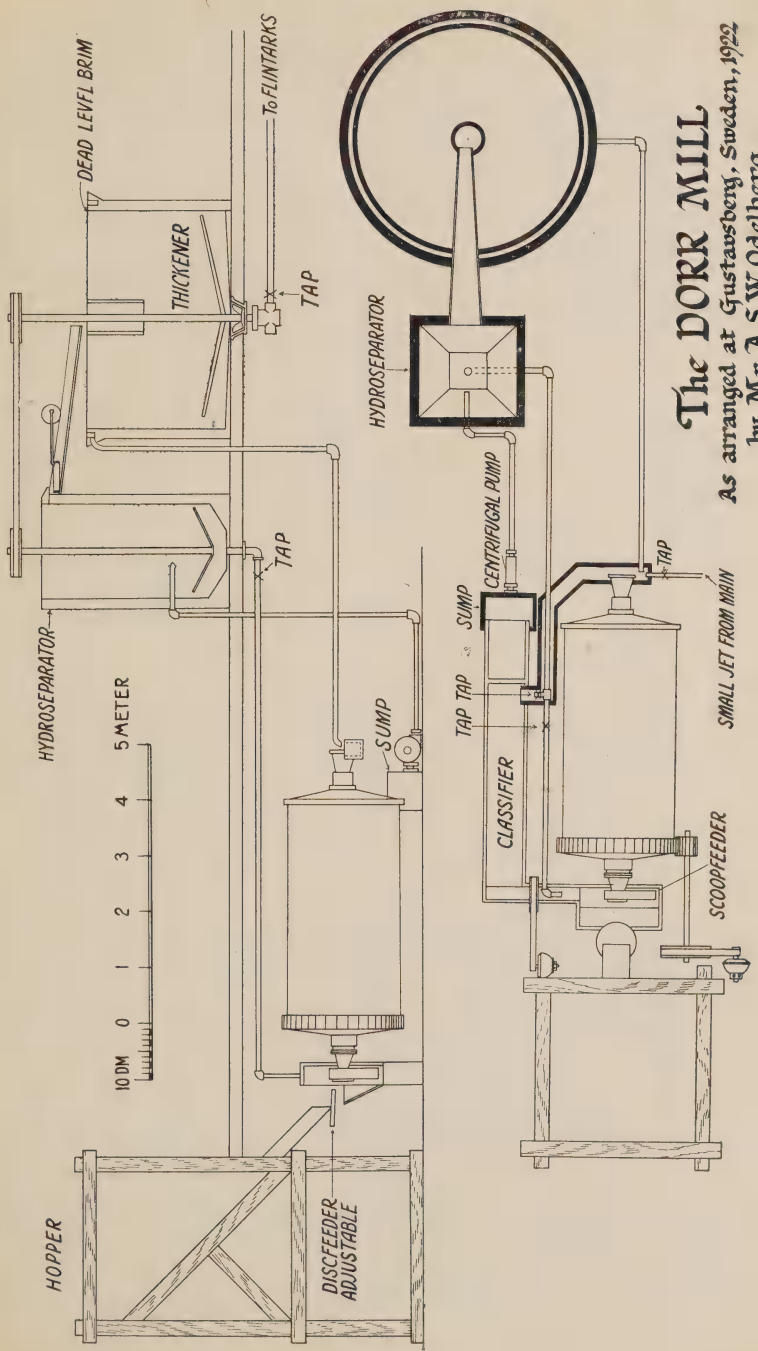
The Dorr Mill:

Charge: 5 tons (4,800 kilograms) in 24 hours.
Power consumed: 537·6 units (or 22·4 units per hour).
Finished product per unit: 9 kilograms.
Fineness: 60% under ·01 m/m.
40% from ·01 to ·03. m/m.

Batch Grinding Cylinder:

Charge: 1,200 kilograms in 14 hours.
Power consumed: 251 units (or 18 units per hour).
Finished product: 4·8 kilograms per unit.
Fineness: 60% under ·01.
28% from ·01 to ·03.
12% from ·03 to ·05.

This shows, the material being the same ($\frac{2}{3}$ flint $\frac{1}{3}$ quartz) in both cases, and crushed to the same grain (1 cm. mesh) before grinding, that batch grinding requires twice the amount of power, if not more, since in the above instance, the elutriation analysis shows that the product is coarser. It also proves the Dorr mill product to be of more uniform grading, or that the batch grinding gives a wider range of particles.


The DORR MILL
As arranged at Gustavsberg, Sweden, 1922
by Mr. A.S.W. Odelberg.
DEAD LEVEL BRIM
THICKENER
TO FLINTARKS
TAP
HYDROSEPARATOR
TAP
HYDROSEPARATOR
CENTRIFUGAL PUMP
SUMP
TAP TAP
CLASSIFIER
TAP
SMALL JET FROM MAIN
SCOOPFEEDER
SUMP
5 METER
4
3
2
1
0
10 DM
HOPPER
DISCFEEDER ADJUSTABLE

According to my experience, the Dorr product is more suitable for making good earthenware, as it is absolutely similar to the flint produced by the old pans in conjunction with "washing-up." It throws some light on the reluctance of English potters to abandon that system.

As to the best speed for the Dorr mill, I have found that by reducing the revs. to 24 per minute you get considerably more output per unit of power, in fact, nearly 25% more, but that in my particular case the total output per unit of time, say 24 hours, is so much reduced, that I prefer to run the mill at the higher speed. Otherwise, I should have to add batch-ground material, which is more expensive to produce, as shown above, and not so good for the ware.

Since my arrival in England, I have had some discussions with several "grinding" experts, and have been strongly advised to install a "Dorr Ball Classifier" in addition to the present classifier. My attention was specially drawn to the fact that, by using only the ordinary classifier, the viscosity of the pulp is so great as to cause the rakes to remove finished as well as unfinished material back to the mill. In reply to my instructions to make an analysis of the raked material, I received a cable from home in reply:

Particles under ·01	8%
,, from ·01 to ·03 ..	12%
Remainder	80%

From this I draw the conclusion that by proper washing in the classifier, I should gain about 13% finished material, which is now returned to the mill, doing no good, and only hampering the output. If this can be attained by the addition of a ball classifier, it is well worth the outlay.

The experts referred to above are of opinion that it is unwise to let the tube mill do all the work. It is better to proceed step by step in reducing the material to fineness, using for instance a Sturtevant rock crusher or rollers and a Ferraris ball mill between the stone breaker and the tube mill. The Ferraris ball mill should grind wet, the pulp from this mill going *directly* to the classifier (to catch material already ground sufficiently fine), and the tube mill should only be fed with "raked material." There is no doubt that by this arrangement the output of the mill would be very substantially increased.

I am afraid that hitherto I have been committing the fault of using the fine grinding machinery for doing coarse work, which is as uneconomical as letting a brain worker do a labourers' work, or in other words, it is as if a Prime Minister were to break stones, which is certainly not true national economy. When I have had an opportunity of testing these ideas, I hope to be in a position to report progress.

In any case, it will be as well to retain the hydro-separator, so as to be able to vary the size of grain of the finished particles. In this

manner the hydro-separator will do its work even better than at present, as the pulp will be much more diluted, hence easier separation of the particles will take place. The work of the pump will also be lightened, as less coarse material will require to be raised. Here I may also mention that the tap under the hydro-separator, which indirectly regulates the speed of elutriation in the hydro-separator, is now made of cast iron instead of brass, which was constantly worn out by the pulp, and required to be frequently replaced. The cast iron seems to last almost indefinitely.

On the last occasion I mentioned that I could not say with certainty what effect the absence of slime would have upon the ware. I can now report it is decidedly for the better.

As to the fear expressed during the discussion of the previous paper that iron would enter into the material from the plant, I am very glad to be able to tell you that I have never had cleaner material than by this process, of which I have now had three years' experience. This is easily explained by the fact that the material is always travelling, during the whole of the process, and that it leaves the grinding plant in a very short time. On one occasion the lining of the tube mill became partially damaged, thus exposing the iron itself to the grinding action, and this over a period of several weeks before repairs could be effected, as I did not want to stop the mill. I would even go so far as to say that I would not be afraid of lining the tube mill with manganese steel plates (as is done in the ochre trade), which hardly ever show any wear, according to what I am told. The whiteness of the material is clearly shown by my samples of ware, the flint and quartz of which are ground by this process.

Apart from such possibilities of perfecting the process, I am convinced that no more scientific and easily regulated method of wet grinding minerals has yet seen daylight, but it must be borne in mind that this grinding plant is indicated only where a large output is required, say a minimum of 50 tons per week, as the work ought never to be intermittent. You will realise that it is suitable not merely for potters' materials, but for any hard mineral insoluble in water. Thus I have had, through the publication of the last paper, numerous enquiries from many other trades, particularly from the ore dressing industry.

DISCUSSION.

Mr. A. G. Richardson (Chairman):—In regard to the Dorr mill, Mr. Odelberg claims one or two important things which are likely to be of special value to us as potters. Amongst these claims are:—the elimination of iron and the greater uniformity that can be obtained as compared with the old pan grinding. If any of the members of the Society doubt those claims, Mr. Odelberg will be glad to answer any questions that may be raised.

MR. C. E. RAMSDEN :—I understood Mr. Odelberg to say that he recommended the adoption of some sort of machine to do the coarser grinding between the crusher and the Dorr mill. Would he be good enough to tell us what kind of machine this is ?

MR. ODELBERG :—I think that is fully explained in the paper. The flint and quartz as it comes from the crusher is about the size of my finger nails ; but before that material is fed to the Dorr mill, it should be in the nature of a fine sand. An edge runner and a pair of rollers is all that is required, but any form of machinery could be utilised for the purpose. I have not yet tried it, but I have been advised to try it, and I am going to do so, for I have no doubt that, by so doing, I shall greatly increase the output of the mill, for the reasons stated in the paper. The recommendation in the paper is : "The Ferraris ball mill should grind wet," and the product of that mill goes direct to the classifier, so that you get the fine in the first milling taken away at once, and only the raked product goes into the tube mill. That is one way of doing it. But I do not think I would go so far as that, because I cannot handle more flint. I think a pair of rollers will do just as well.

MAJOR B. J. MOORE :—Does the new body stand up to crazing quite as well as the old ?

MR. ODELBERG :—We have less crazing with the new body, and also less peeling. It is altogether better balanced as regards the glaze than the old body was.

With regard to the whiteness, I do not think you can expect anything better. I am particularly proud of some of the samples which you see before you on the table. These have been made from our ordinary body. It contained very much ball clay and yet it is particularly white. There is not the slightest doubt that the introduction of this new form of grinding has considerably improved our body. Of that we ourselves are convinced. We have now attained to the same results as you have attained over here through centuries of experience of washing up by the old pans, which gave a very much more uniform product than the batch grinding cylinders did, merely because, in the latter, you got too much fine stuff, which has a prejudicial effect upon the making of the ware. I am quire aware that the best earthenware in the world—which is made in Staffordshire—is still produced by the old pan grinding process.

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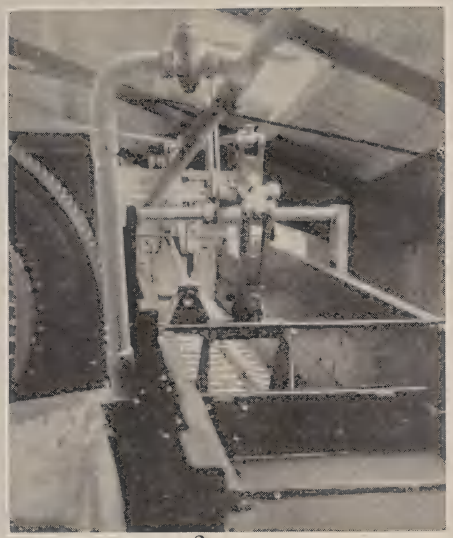

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Figs. 1-3. Views of Dorr Mill plant at Gustavsberg, showing centrifugal pump, feeder and classifier.
Fig. 4. Felspar sorting works at Margretelund. Fig. 5. Pneumatic boring in the Idsätra mine (150 ft. deep).
Fig. 6. Stacks of felspar at the Idsätra mine.

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XXIII.—The Swedish Felspar Industry.

By A. S. W. Odelberg.

SWEDEN is known to be very fortunate in having particularly pure supplies of different minerals. This is true especially of her iron ore, used for making high-class steel with a reputation of many centuries, and also of her quartz and felspar which have, of course, been of commercial interest only in modern times.

The Felspar Industry is fairly widely scattered over the country, but the largest outcrops are to be found in the Baltic Archipelago in the neighbourhood of Stockholm. Here are the celebrated Ytterby Mines, which are still working.

In more recent times, about 1893, in carrying out a drainage scheme on the small farm of Aettaro, belonging to the large estate of Margretelund, the then Proprietor being the Prime Minister of Sweden, Count Akerhielm, an outcrop of particularly pure potash felspar was discovered. When the Ceramic Society visited my country in June, 1922, I particularly wished to arrange a visit to these Mines, as being the most representative of the Felspar Industry, but, unfortunately, time would not allow, especially as the mines are somewhat off the beaten track.

The Felspar produced in Sweden is chiefly orthoclase, and in these particular mines no other variety occurs. In a few of the other mines, albite (soda felspar), is also found, but in minor quantities. It has come to my knowledge that the more prominent German insulator manufactories are very eager to get supplies of this albite, as they are of opinion that either a mixture of albite and orthoclase, or albite alone, improves the insulating efficiency.

The mines at Margretelund are now worked by a limited company, Margretelunds Gruve A.-B., founded in 1915, of which Bergsingeniör Harry Nathorst is the Managing Director. He is an expert on geology and mining of considerable reputation. Since he has taken over the management, it has been put on quite a scientific footing.

The average production per annum during the last 15 years has amounted to 9,500 tons. The greatest annual production shows 14,400 tons of which 8,000 tons are first quality felspar.

The felspar produced at present is divided into two qualities. First quality extra, of white appearance, and first quality red, of a pinkish colour. Along with the felspar an exceedingly pure white quartz occurs. The analyses of these three products are as follows :—

	Felspar, white, extra. First quality. %	Felspar, red. First quality. %	Quartz, white, First quality. %
SiO_2	65,68	65,44	99,45
Al_2O_5	18,02	19,37	trace
FeO	0,12	0,32	—
Fe_2O_3	—	—	0,17
CaO	0,16	0,24	trace
MgO	—	trace	0,07
Loss on ignition ..	n.d.	0,14	0,12
K_2O	13,46	12,56	—
Na_2O	1,90	2,54	—
	99,34	100,61	99,81

At the spot where the first felspar was discovered it was at first mined by open air quarrying with an area of only 300 square metres. On penetrating deeper, the area continually increased, and at the present depth is 3,000 square metres. The mine at this spot, which is called Härsbacka, has constantly been worked during a period of 29 years, and has been abandoned a few years ago, until new machinery capable of lifting from greater depths can be installed. To cut a long story short, many hundred thousand tons of spar and quartz still remain in this mine, which for quantity and quality is quite unique.

As the result of very careful geological and topographical observations, Mr. Nathorst came to the conclusion that there must exist a large quantity of felspar hidden by layers of earth about half a mile from the Härsbacka mine at a spot called Idsätra. After only one day's digging, it was found that his anticipations were correct. This mine is called "Idsätra Källaregneva," and the yield to be expected from it is perhaps just a trifle smaller than that of the mine at Härsbacka. The Idsätra Mine is particularly interesting on account of the size of the pure felspar masses. Whereas at Härsbacka, each mass seldom yields more than 4,000 tons, a single mass at Idsätra has up to the present date yielded not less than 22,000 tons, of which 16,800 tons are of first quality and still the bottom of this mass has not yet been reached.

The mines are equipped with a 100 H.P. Diesel Motor, driving an air compressor giving enough power both for the lift and boring machinery. To pump water from the mine, electric current is generated from a 15 H.P. steam turbine with dynamo, which receives steam from the boiler warming the air for the pneumatic machinery.

The mineral is loaded in trucks, taking a ton and a quarter, and brought to the surface by a lift with counter-weight. The large pieces of pure mineral are sorted in the mine, but the smaller pieces are sorted at special works about half a mile from the mine close to the point of shipment. The usable mineral

coming from the mine is stored in piles from which it is either taken direct to the ship or to the previously mentioned sorting works (smaller pieces only as previously said). The railroad from the mine to the point of shipment or sorting, as the case may be, has a length of about one mile, and the mineral is carried in tipping trucks taking two and a half tons. These trucks have ball bearings made by the famous S.K.F. Works at Gothenburg (visited by the Ceramic Society), and are drawn by a small petrol locomotive of 6 H.P. of the Austro-Daimler type, taking 5 trucks at a speed of 6 miles an hour. This system of transport works very economically, the cost of petrol for moving 1 ton of mineral amounting to only a half-penny.

The piles in front of the stonebreaker hold 70 tons, and the capacity of the present sorting plant is about 70 tons per eight hour day, but with extra labour an output of 100 tons can be reached. This machinery, as well as that for loading the ships, is driven by a raw oil motor of 35 H.P.

The shipping quay is 5 metres above water level, and the depth of the water alongside is also 5 metres or about seventeen feet, thus allowing very large ships to be berthed. The shipping capacity per day is 200 tons.

England is favoured with the finest clays in the world for making pottery. Sweden on the other hand has, perhaps, the best spar, and the exchange of these commodities is to our mutual benefit.

XXIV.—Porcelain for High Tension Insulators.*

By K. H. Reichau, D.Ph.

A NUMBER of years ago, when the electrical industry first began to employ porcelain as an insulating material, it was only used to a very moderate extent, although the porcelain industry could look back upon a process of development stretching over a period of more than a hundred years. The knowledge and experience gained during this period, although chiefly devoted to discovering how to produce articles of general utility and artistic value, was sufficient to satisfy the very modest demands of the high tension electrical industry at that time.

The high tension development really began with the transmission of power from Lauffen to Frankfort, in 1891. Since then the situation has fundamentally altered. The facility with which the high tension industry has been able to utilise practically all forms of power supply and the elasticity with which it enables central power generating stations to distribute their supply over a very wide area have interested industry and capital to an equal extent. When it was discovered that the economy of electrical energy distribution increased with the voltage of the distribution, the last decade witnessed a phenomenal increase in the voltage of transmission lines up to the modern maximum of 220 kilovolts, and thereby to the realisation of power supply stations lying several hundreds of kilometres from their customers. At the beginning, high tension electrical engineers confined their attention to the development of suitable shapes for porcelain insulators and were content to obtain the porcelain as a finished material without further development to suit their special requirements; but gradually, owing to disillusionments and costly experiences, interest is beginning to be taken not only in the form of the insulator, but also in the material itself, for two fundamental reasons. First, the porcelain insulator must ensure the absolute electrical and mechanical reliability of the high tension line under normal service conditions. Since the tendency in normal high tension work is to protect valuable machines and apparatus in the central and sub-stations in as complete a manner as possible from disturbances produced by switching operations and atmospheric conditions, the brunt of these disturbances, which are generally of high frequency, falls on the transmission line itself and must be carried by the porcelain insulators without breakdown or danger to normal operation. In this way, two completely separate industries, namely, the electrical and the ceramic, are brought into close contact with each other, and the present appears an opportune moment to raise the question

* The author is indebted to Mr. G. McKerrow for valuable assistance with the translation of this paper. (Translated from the German).

of how to judge the value of high tension porcelain and the present position of this art.

If the final problem of the production of high tension porcelain only consisted in making a silicate insulator of sufficiently high mechanical and as high dielectrical strength as possible, it could be very simply solved, since any insulator produced by pressing or casting suitable glass material would satisfy these requirements probably better then the best hard porcelain. Such glass insulators, which in former years were used for some time for lower voltages, have not proved at all suitable, firstly because the alkaline earths and alkalis, present as double silicates in the glass, break up very easily under the influence of the atmosphere and cause leakage from the insulator to the earth; secondly, because thick walled glass insulators of this type, even if they are made in the most careful manner possible, are subject to internal stresses which are developed gradually by variations in temperature and, finally, cause mechanical splintering of the insulator; and lastly, because the glass material, although it may have sufficient resistance to static stresses, has proved in practice to be too brittle and inelastic to carry the dynamic stresses. Electrical engineers, therefore, took objection to employing glass insulators, especially in high tension systems, after many experiments which ended in failure, even although such glass insulators possess high mechanical and electric strength and are of a completely non-porous texture; and it is clear that, for high tension, the value of the insulators must be judged from other points of view and that the electrical strength alone is not of decisive importance, although it is often considered to be so, even in technical circles.

The best thin porcelain, such as is supplied commercially for first quality articles for every-day use or for chemical ware, in which it reaches its highest point of excellence, possesses all the recognised valuable properties which the electrical engineer demands for high tension insulators. During the process of manufacture it can be easily worked into any desired form; it can be produced in thick, dense sections, which may be covered either with white or coloured glaze, so that both the glazed and unglazed surfaces are well able to withstand chemical reactions, either from acids or alkalis. In comparison with the better sorts of glass, it is much less sensitive to quick changes in temperature and it is sufficiently elastic. It possesses great mechanical strength, both against tension and pressure, and its dielectric strength is high, so that porcelain plates 1 cm. thick ($\frac{3}{8}$ in.) in a homogeneous electric field of normal 50 cycles A.C. only break down under a tension of 90,000 volts.

In spite of all these salient advantages of porcelain, which make it appear most suitable as an insulating material for high tension transmission, complaints increase from year to year in technical papers all over the world about breakdowns in operation and about serious troubles which are due to faulty manufacture

of transmission line insulators. The reasons for these failures, if they are not caused by the expansion of cement and the like, must be sought for in the porcelain material itself, and the question of the suitability of porcelain for high tension purposes is clearly, therefore, a question of material.

The most common complaints refer to the porosity, that is to say, to insufficient density of the porcelain body. First of all, it must be agreed that material which is not absolutely dense is no porcelain in the true ceramic sense, but only a form of earthenware, and it seems quite unjustifiable for manufacturers to put porous material on the market under the name of porcelain. Such porcelains show a granular earthenware type of fracture, because the individual components of the body, that is to say, the quartz, china clay and felspar, are only fitted together by the molten felspar and the degree of porosity depends, therefore, on the degree of the fritting. If the material is coarse-grained and not sufficiently fritted (vitreous), there will be a greater or smaller number of large cavities communicating with each other and with the inside of the material, so that if there is the slightest defect in the glaze or if, as is always the case, there are a certain number of unglazed parts on the insulator, the atmospheric moisture is able to penetrate into the interior of the body, and the current which consequently passes warms up the insulator, which begins to glow and hiss when the transmission line is enveloped in clouds or rain ; finally, after a short time in service, the insulator bursts. On the other hand, if the material of the insulator is more thoroughly fritted, owing to the grains of the body being finer or to being fired longer or at a higher temperature, or to the greater content of felspar, then the individual small or large spaces on the fractured surface of the insulator do not communicate either with each other or with the inside of the body. An ink line drawn on a freshly broken surface of earthenware-like material spreads owing to capillary action on the granulated surface, which is similar to sandstone, without penetrating to any great extent into the inside of the material. Also any attempt to force a solution of fuchsin in alcohol into the inside of the piece by means of high pressure, even if applied for a long time, fails to produce any defect. An insulator of this type will, however, always remain a weak link in the transmission line, and through gradual corrosion of the surface it can confidently be expected to break down after longer or shorter service. The first property which must be required from porcelain material which is suitable for manufacturing insulators, is, therefore, that it should be absolutely dense, well glazed and fracture neither in a granular manner nor in a manner similar to sandstone.

This first and principal requirement of complete absence of porosity with a well-glazed and non-granular fracture, which can be so easily achieved for household ware, becomes one of the most difficult conditions to realise, since one is concerned with the pro-

duction of porcelain pieces of thick cross-section ; it would not be going too far to assess the quality of the work of a porcelain factory by determining how thick a porcelain, fulfilling the above-mentioned conditions and free from blemish, it can turn out in quantities. A piece of porcelain of this sort in the shape of a solid cylinder of 6 or 8 centimetres diameter and of the same height, not only provides information as to whether the body has been correctly mixed, but also gives the most valuable information on the method of firing and the maximum temperature obtained, in addition to the period for which this maximum is maintained.

Fig. 1. Fractures of genuine porcelain compared with that of "over-fired" porcelain.

The three porcelain samples in Figure 1 show that, for imitating or producing a porcelain of this sort, neither a knowledge of the chemical and rational analysis nor of the physical requirements, that is to say, a knowledge of the fineness of the grain or the time for which the body has been milled, is sufficient. The three cylinders were exactly alike in the green and in the biscuit stage, and they were built up chemically almost and rationally entirely alike from a body composed of 53 per cent. clay substance, 29 per cent. silica and 18 per cent. felspar ; furthermore, all three bodies were absolutely identical as regards the physical size of the grain and the fineness of the material in the green condition, and all three bodies were fired in the same sagger at the same time in the same furnace under exactly the same atmospheric conditions up to Seger cone 16. In addition, when examined in thin sections, none of the three finished pieces of porcelain contained appreciable traces of free silica, but only the first body formed a true hard porcelain with a characteristic smooth fracture, as can be seen from the wavy appearance of the fractured test piece. Both the other bodies show more or less strongly the result which would have come out by trying to vitrify the more or less porous insulators by higher or

longer firing. At the outside near the surface they would have become dense, probably full of holes and bubbles on the upper surface and at the same time they would have been subjected to pressure outwards from the inside. In order to prevent this tendency to disruption, the more or less porous insulators described above had been fritted very carefully, so that they possessed mechanical and electrical strength just sufficient for the usual inspection test.

It would appear, therefore, that it might be preferable to use some other method for producing the dense porcelain, namely, to raise the flux content of the body in order to increase the fusion of the mass, and, in this way, the density of the piece. Figure 2 shows three bodies containing 30, 35 and 40 per cent. of felspar respectively, which were fired to different maximum temperatures,

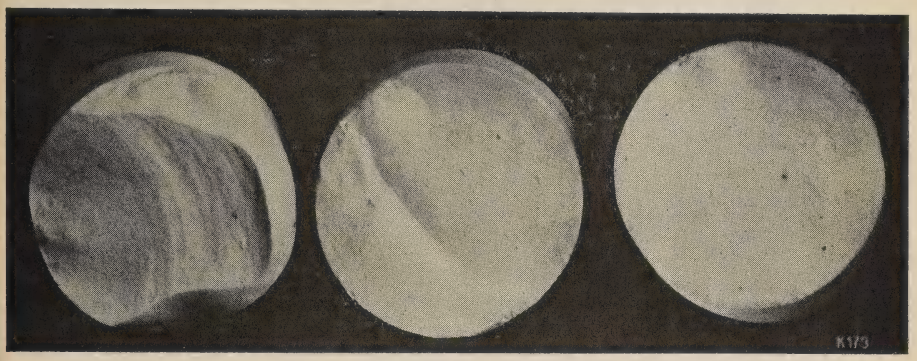

Fig. 2. Fractures of three porcelain cylinders with increasing content of felspar.

but were otherwise correctly built up and, physically, absolutely similar. The dense, wavy fracture of true hard porcelain disappears gradually with the increase of felspar content. It is replaced by the smoother felspar fracture and lastly, by the smooth, almost glassy-like, fracture of felspar glass. Bodies of this type, with a high content of felspar, cannot, for a number of reasons, be employed for high tension insulators. In the first place, such short bodies cannot be easily worked in the green condition. Also, it is impossible to produce articles which are thick in places and thin in others, because the thin portion of the insulator, such as the thin wall of a groove, begins to melt before the thick portion has been completely fired and, lastly, insulators of this type, owing to their high content of silica felspar glass, are very sensitive to temperature changes. This raises the second very important requirement which high tension electrical engineers look for in porcelain, namely, the ability of the material to withstand rapid, even though limited, changes of temperature.

In general, for equal coefficients of expansion, coarse-grained materials are appreciably less sensitive to sudden temperature changes than fine-grained materials, since it is appreciably harder to equalise out the internal strains inside fine-grained material. An earthenware body has much higher resistance to temperature change than a glass body of the same thickness, so that more or less porous porcelain with a coarse-grained sandstone-like fracture, although it contravenes the first requirement of high tension porcelain, namely, that the body should be a dense one, can be used to form insulators, which would fully satisfy the second requirement. Therefore, all insulators with an earthenware-like granular fracture represent technically a compromise between these two requirements. In other words, they strive to fulfil both conditions at the expense of each other and fulfil both in an unsatisfactory manner. They are in every respect, both as regards the composition of the body and also in the matter of maximum temperature of firing, a typical product of empirical experiment. If the high tension electrical engineer had built his transformers and machines on similar compromises, he would probably to-day not have progressed beyond the first 10,000 to 20,000 volt transmission line.

If, therefore, the large cylinder mentioned previously, of about 6 to 8 centimetres diameter, is to represent a measure of the ability of a porcelain works to manufacture suitable material, it must not only have an absolutely dense and impervious body, but also great resistance to rapid changes of temperature. It must combine, therefore, certain properties of glass as far as density is concerned and certain properties of earthenware as far as the capacity to withstand temperature change is concerned. Both these requirements can only be satisfactorily realised at the same time by a material which is in all respects completely homogeneous. A porcelain completely homogeneous in this way may be called in the technical sense a "genuine" porcelain.[1]

The first two requirements of the high tension electrical engineer amount actually to this; the material from which the high tension insulator is to be made must be genuine, or as far as possible, genuine porcelain. In the course of further examination it will be shown that, with the fulfilment of this requirement, a great many other requirements, such as high mechanical strength, both compressive and tensile, great elasticity and high dielectric strength are automatically fulfilled, and lastly, a further very important asset is obtained automatically, namely, the absolute chemical stability of the material and immunity from ageing.

It is perhaps suitable at this point to add a few remarks on the production of porcelain itself and on the points which differentiate "genuine" porcelain from the material commonly obtainable commercially. In building up a body, the raw materials, china clay,

[1] For references see page 299.

silica and felspar, are generally used in the proportion of 50 to 25 to 25 and are as finely ground as possible; water is added to them until a plastic mass is obtained. In other words, the ability to shape objects of clay in the ceramic industry proper—in sharp contrast with the corresponding process in the glass industry—depends upon the colloidal portion of the alumino-silicic acid being in a hydrated condition. After the piece formed in this way has been sufficiently dried, it is thoroughly fired in the oven. During firing at about 500° china clay gives up its water content—100 per cent. of china clay contains about 14 per cent. of water—and breaks up molecularly into silicic acid and alumina at about 900°. It appears that a portion of the free silicic acid unites again with the alumina, causing the development of heat and forming an amorphous silicate with a composition $Al_2O_3SiO_2$, that is to say, an amorphous sillimanite.

At about 1,100 to 1,200° the felspar added to the body melts to form a very viscous glass and, as the temperature rises, further acts on the other components, namely, on the silicic acid, the alumina and the amorphous sillimanite. In order to allow this action to take place as intensively as possible, the body must be correctly prepared in several different respects. First of all, the components must be present in the right form and in the right size of grain, so that the individual parts present as far as possible a molecular surface for the attack of the solvent felspar; but, at the same time, the material must be able to stand both a high and lengthy firing. The higher the firing temperature rises and the longer it can be maintained, the better is the body, since only in a body of this kind can the felspar work intensively on all the individual components of the mass. This dissolving process very closely resembles in its character organic esterification, which is also a function of time and temperature and often requires, as in the case of the complex aldehydes, several days' time to complete its action[2]. The fluid molten felspar dissolves the molecular residue of silicic acid left from the breaking up of the china clay and then attacks the free silica contained in the material. It more or less completely dissolves it, depending on the size of surface presented by the silica for solution, and it changes the impervious silicate into a desmotrope crystalline form by mass action. In this complete chemical process the felspar behaves, all the time the firing is at its height, like a strongly unsaturated compound, a point which Seger realised. A thin section of the finished porcelain body shows unmistakably whether this reaction has been more or less realised. If the thin section still contains a large number of free pieces of quartz of a splintery shape or many angular broken fragments, one can rely with considerable certainty on the body of the porcelain being more or less porous or containing an excessive amount of felspar. If, however, the reaction has been complete[3], the section will reveal a homogeneous, glassy body with numerous

small felt-like networks of sillimanite crystals, sometimes with lattice structure. A porcelain of this type is, in all respects, homogeneous and in the technical sense genuine porcelain.[4] Only in quite isolated cases do a few small well-rounded quartz grains occur in the felspar glass body of a porcelain of this kind, and the sillimanite crystals point from all sides towards these grains of silica. Around the silica grain there lies a broad glassy ring of felspar glass saturated with silica and completely free from sillimanite crystals, in which, owing to the high saturation of the felspar with silicic-acid, dissolved from the quartz grain, the conditions[5] necessary for the formation of sillimanite were no longer given. (Fig. 3)[6].

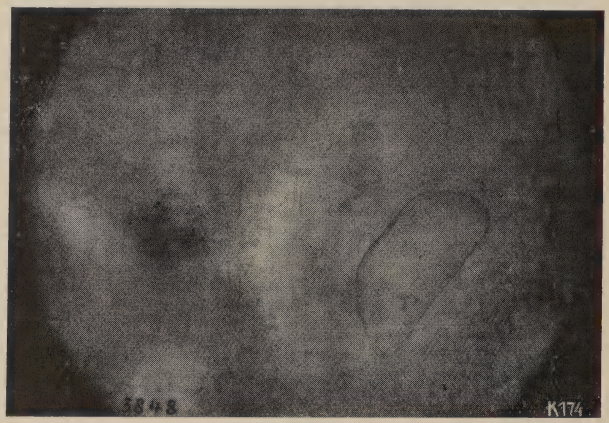

Fig. 3.
Photograph in blue light of silica grain in process of being dissolved in true porcelain. × 800.

From the above considerations it is now clear that the characteristics of genuine porcelain bodies cannot be recognised by chemical or rational analysis or physical composition or by determining the amount of free silica present or not present, but only from careful examination of the internal structure of the finished porcelain article, which has been fired from any given porcelain body. There are as many genuine porcelains as there are chemical and rational analyses for porcelain bodies; and there is no point in discussing the properties to be expected from a porcelain of given composition unless the conditions necessary to produce genuine porcelain are provided for in compounding the body.

In the well-known triangular co-ordinate system (Fig. 4), there is indicated by the centre of the circle drawn on the figure the composition of that body which, by virtue of its central position with a composition of 50 per cent. clay substance, 25 per cent. silica, and 25 per cent. felspar, represents the mean for mechanical

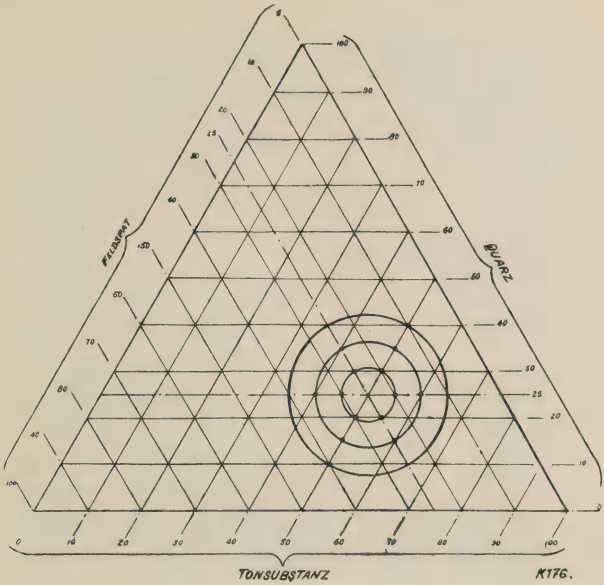

Fig. 4.
Position of genuine bodies in the Ceramic three-phase system.

and electrical strength and resistance to temperature changes.

Only on the assumption that all the bodies contained in this diagram have been compounded in such a manner as to produce genuine porcelains on firing, can the body composition be varied effectually to attain the end in view; for instance, to produce porcelains having high mechanical or electrical strength, great resistance to abrupt changes of temperature, or special translucency.

The rational compositions indicated in the diagram represent three groups of bodies. In the first the clay substance is kept constant while the silica and felspar are varied; in the second group, the silica content is kept constant while the clay substance and felspar are varied, whilst in the third group the felspar is constant and the clay substance and silica are varied. With the exception of the bodies which have been "shortened" considerably, composed of ·

20 per cent. Clay Substance.	55 per cent. Silica.	25 per cent Felspar.
30 ,, ,,	45 ,, ,,	25 ,, ,,
20 ,, ,,	25 ,, ,,	55 ,, ,,
30 ,, ,,	25 ,, ,,	45 ,, ,,

which are always liable to crack while being worked, all these bodies, if suitably compounded, may be made up into a highly plastic raw condition.

It is clear, of course, that all these bodies must be fired to different maturing temperatures, that is to say, the final tem-

perature must be from 150° to 200° below the melting point of the body, so that it can be maintained for a sufficient length of time. For all bodies, with the exception of the two with 45 per cent. clay substance, the maximum temperature for those in the area enclosed in the circle is at least as high as Seger cones 14 and 16, and all body compositions lying outside the encircled area hardly interest porcelain manufacturers at all, in so far as they are concerned with producing genuine porcelain for high tension electrical work.

The more porcelain differs in its structure from genuine porcelain, the more does it become illusory to rely on working on the above triangular co-ordinate system, since in this case the rational composition of the mass is no longer the sole deciding factor for the properties of the finished porcelain, but quite different matters, such as the size of grain, the presence of free silica, etc., must be taken into account. Elimination of such disturbing influences forms, however, an appreciable part of the preliminary requirements, which must be taken into account in building up the body, in order to obtain a genuine porcelain. These preliminary requirements are very numerous, but amongst them one, in particular, is attracting the special attention of a very wide circle, namely, the correct choice of the grain size of free silica contained in the body. Of late years papers have been published which create the impression that the total absence of free quartz in finished porcelain

Fig. 5a. Velocity 0·0—0·2 mm. per sec.

Figs. 5a to 5e—Fractured surfaces of porcelain cylinders of the same shape and made in the same way but containing silica of different grain sizes, graded by elutriation. (Schöne system).

Fig. 5b.
Velocity 0·2—0·7 mm. per sec.

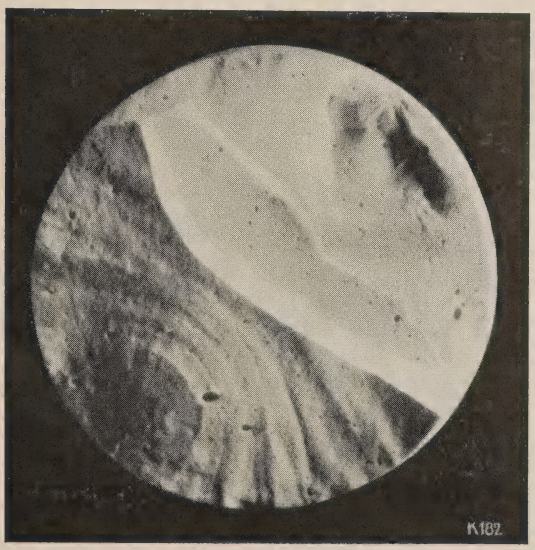

Fig. 5c.
Velocity 0·7—1·5 mm. per sec.

Fig. 5d.
Velocity 1·5—3·5 mm. per sec.

Fig. 5e.
Residue above 3·5 mm. per sec.

decides whether it is genuine porcelain or not[7]. A porcelain body which still contains quite a considerable quantity of free silica, even if it has been correctly fired, may, under certain conditions, approximate to a genuine porcelain much more closely than a body which contains only traces of free silica, even if the porcelain has been correctly fired. However, Fig. 5 shows how important the grain size of the silica used in forming a body may be for the finished product. All the porcelain samples shown in this figure have the same rational analysis (53 per cent. clay substance, 29 per cent. silica and 18 per cent. felspar), and were fired at the same time and in the same saggar at Seger cone 16. The only difference between them is the grain size of the quartz, which was obtained from washing a practically 100 per cent. quartz, which had been ground for about 50 hours in a ball-mill, in a Schoene apparatus and using the fractions obtained at velocities corresponding to 0·2, 0·7, 1·3, 3·5 mm. of water and the residue left at the highest speed. Otherwise the conditions governing the production of the bodies were absolutely identical. From the purely chemical point of view, the consideration of the grain size of the silica in the body amounts to nothing more than a consideration of the lowering of the reaction and melting temperature due entirely to the degree of dispersion, and the fulfilment of the further preliminary condition, that the components contained in the body will operate as far as possible like fluids, as regards their vapour pressure, at the melting point, or, in other words, the removal, as far as possible, of all disturbances due to hysteretic phenomena in the phase equilibrium of the body constituents at the maturing temperature. The fulfilment of this preliminary condition is important, but in no way sufficient in itself for the production of genuine porcelain. However, the above figure shows in the clearest manner how important is the influence of the grain size of the silica on the character of the finished porcelain.

The first and fundamentally the most important requirement which must be demanded from porcelain, if it is to be suitable for high tension electrical apparatus, is, therefore, that it should resemble in character, as far as possible, a genuine porcelain. The previously mentioned porcelain cylinder should be as large in diameter as possible. It should be completely dense and it should be able to withstand temperature changes over a long period. The thin section should not show individual isolated clusters of sillimanite (which can very easily be produced), and at the same time many splintery fragments and much free silica, but it should show a thick felted network of sillimanite crystals embedded in a homogeneous glassy groundmass with either no free silica or, if for any reason the presence of free silica is essential, only traces of silica grains having completely rounded edges owing to the solvent action of the felspar. At the same time the cylinder must be thoroughly well fired and matured throughout, so that two thin

sections, one taken from the outside of the cylinder and the other from the middle, show exactly the same appearance as described above.

Practical tests on two Hewlett suspension insulators prepared from such a body and measuring about 22 cm. in diameter, gave the expected results. The electrical breakdown strength of the insulators at 50 cycles A.C. under oil was high in comparison with those made by numerous other manufacturers; the insulators resisted rapid quenching from boiling water into water at 10°, *i.e.*, a temperature change of 90°, and when broken mechanically, they showed absolutely dense fracture, which had completely lost the splintery fracture characteristic of glass. At those points where the fracture had been produced by a sudden blow with the edge of a hammer, the fractured surface showed circular waves as a sign of the homogeneity and elasticity of the material. On the fractured surface of the first sample in Fig. 1, this characteristic break can be clearly recognised. Both thin sections were identical and showed the characteristics described above.

The third very important requirement which the high tension electrical engineer must demand of porcelain specially suitable for his purpose is, that it should possess a sufficiently high di-electric strength. For numerous reasons, a thin unglazed flat plate, about 10 cms. by 10 cms., should be employed for this form of test. A plate of this description about 3 mm. thick shows better than any other form of test piece whether the material used for building up the body stands the firing well. If such a plate can be well and evenly fired without distortion, it is a proof that the body is homogeneous throughout, that it has uniform and simultaneous shrinkage, and that insulators made from such material will certainly be free from internal stress. Further, the electrical testing of a thin sheet of the material is a much more reliable way of determining the points which are weak and unable to resist electrical strain, than if one tests a piece of thick cross-section. In order to obtain a reliable value for the porcelain material, the plate should be tested in the unglazed condition. The actual testing of the plate can be best of all carried out in a homogeneous field between electrodes, which are not too small in size, in order that a suitably large surface may be exposed to the electrical stress and a true mean value obtained. For this form of test it is advisable to use a form of apparatus in which the magnitude and direction of the electric field can be easily determined and with which non-homogeneous points in the material and consequent disturbances in the field can be easily detected[8]. The electrodes are circular in shape, polished to an even surface and well rounded at the edges. They are about 6 cm. diameter and have a surface of 30 sq. cms. They are fastened in porcelain plates (see Fig. 6), that is to say, in material of the same di-electric constant as the sample test piece. In order to get a reliable di-electric value from the test, the air between the electrodes

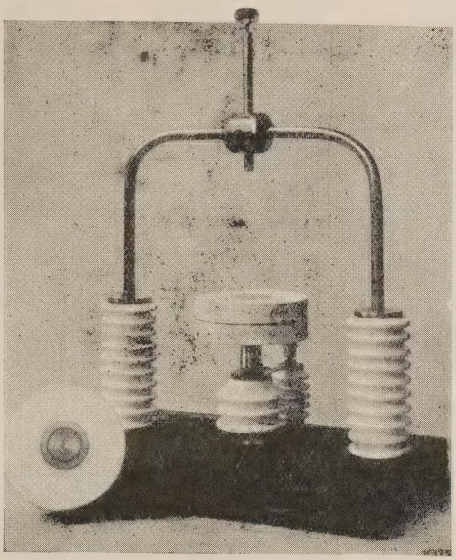

Fig. 6.
Apparatus (spark gap) for testing the breakdown strength of porcelain plates in a homogeneous electrical field.

is replaced by a material of equal di-electric constant ; fresh aniline oil is suitable for this purpose. In assembling the apparatus the groove in the fixed electrode between the brass plate and the porcelain bush is first of all filled with aniline oil (E=7). The groove in the upper electrode is filled in the same way. The porcelain plate, which has been dipped in aniline oil, is then laid on the latter electrode, and this electrode together with the porcelain plate, pressed firmly against it, is then turned over and the free surface of the porcelain plate slipped over the lower electrode. The upper electrode, and with it the porcelain plate which is to be tested, is then pressed into the correct position by means of a guide rod. As a mean value from 6 plates of porcelain tested in this manner, each of about 3 mm. thick, the dielectric strength was found to be 18,200 volts maximum per mm., or 12,900 volts effective, and when thicker plates of genuine porcelain were tested a remarkable proportionality was found between the thickness of the plate and the breakdown voltage, which testified to the homogeneous nature of the material. This value could have been considerably increased by building up the porcelain in a different manner by increasing the glass basis in comparison with the content of clay substance. However, for reasons which have been described above, the high resistance of the material to quick temperature change would have suffered. In the above figures the influence of the warming effect on the breakdown strength was not taken into account.

The fourth and last requirement which high tension electrical engineers should demand from porcelain material is of a purely mechanical nature. The material should be as capable of resisting tensile, compressive and impact stresses as possible. In order to obtain an idea of the importance of these figures for strength in their application to ceramic products and in order to appreciate their inner significance for porcelain, the following experiment serves as an interesting example. Granite containing considerable silicate, which, owing to weathering of the felspar in it, has become rich in clay substance and which, therefore, contains all the components necessary for forming the raw porcelain body, is ground in a ball-mill to different degrees of fineness, that is to say, for about a quarter of an hour first of all, then for about 3 hours and lastly, for about 50 hours. The separate milled products, which are chemically identical and only differ in the grain size, are then placed in the hottest part of a porcelain oven in a porcelain dish. The material which has been milled for a quarter of an hour remains coarse-grained and sinters only on the edges of the grains; the material which has been milled for three hours unites considerably better and at individual places fuses into a solid green mass, while the material which has been milled for 50 hours fuses into a green, dense but very brittle glass. Coarse-grained materials are, therefore, appreciably better able to withstand firing than fine grained materials of exactly the same chemical composition. If the fused materials are then broken up, the material which is only fused along the edges, disintegrates comparatively easily, while the glassy fused material strongly resists fracture. The mechanical cohesion of the coarse-grained material is, therefore, considerably less than that of the fine-grained.

These results may be applied directly without further consideration to the behaviour of ceramic bodies and the porcelains fired from them. The specific gravity of genuine porcelain does not vary to any considerable extent from that of other porcelains, so that this property does not provide any measure of the quality of the porcelain. This is due to the fact that the considerably greater shrinkage on firing of genuine bodies is compensated for by the somewhat lower specific gravity of genuine bodies in the green and biscuit condition. If, however, a thin section is examined under the microscope with gradually increasing magnification, the difference between genuine and any other type of porcelain may be appreciated at once. The edges of the particles of the individual components of the porcelain, which appear under a magnification of 50 times to lie close together without any form of connection, vanish very quickly in the genuine porcelain until they can no longer be detected with a 300 to 500 magnification. For non-genuine porcelain, these edges of the individual grains remain clearly detectable under all magnifications and the ingredients only appear to be fused together by a glass more or less rich in sillimanite. In

the case of a genuine porcelain, the chemical process previously described in porcelain formation has been carried to completion all the components having participated in the same way as the finest ground silica granite in the above experiment, whilst in other porcelains this process has only been effected in places where the conditions for its completion happened to be present. This is specially the case in the neighbourhood of points which are rich in felspar, just as was the case with the coarsely ground granite of the above experiment. The genuine porcelain is, in comparison to the non-genuine, homogeneous throughout its structure and, therefore, from preliminary considerations, is superior in its mechanical properties. As experience has borne out, it is to be expected that, from a mechanical point of view, a porcelain is the more valuable the more its structure approaches genuine porcelain. Herein lies the true reason for the experience found by expert firemen of porcelain from long years of practice, that a body, and therefore, a porcelain also, is of better quality the longer it is able to stand the maximum temperature of the porcelain kiln.[9]

When considering the figures obtained from the mechanical tests on porcelain under tension, pressure, and impact, due regard must be paid to their relative importance. The greatest value must always be placed on the result of the tensile tests of the material, since these tests form a measure of the manner in which the individual porcelain molecules formed from the various components during the process of manufacture are held together. The remaining figures should be considered according to the mechanical stresses which different types of insulators will have to withstand in practice. The importance of these figures is, therefore, relative. For high tension transmission at a pressure higher than about 40,000 to 50,000 volts, the chain type of insulator is employed practically exclusively in modern practice, either of the Hewlett suspension or cap and pin type. The porcelain pieces between the loops on the Hewlett insulators are, apparently, principally under compressive stresses, while the porcelain enclosed between the cap and the pin on the cap insulator has to withstand force in two directions, so that in this case the porcelain is under shearing stress. These purely static forces acting on the insulators, which are determined by the mechanical load of the transmission line at rest, are converted into much more dangerous dynamic stresses, as soon as the transmission line begins to swing under the influence of storm or rain. If the material in question does not possess sufficient strength to withstand these stresses, that is to say, if it is brittle like glass, then, in spite of its great ability to resist static stresses, quite small impact stresses will destroy it. It, therefore, seems correct to place particular weight on the result of the impact test as a measure of the value of the mechanical properties of the porcelain intended for Hewlett and cap insulators, although it is difficult to interpret the results of the impact test on

porcelain in a similar manner to tests on metals, and in this case to place the lowest value on the result of the purely static tensile tests. It is, however, inadmissible to apply this reasoning to other types of insulators, as, for instance, to supporting insulators, which will only be submitted to compression. So that, according to the purpose for which the insulator is required, the composition of the body of the porcelain must be varied.

For practical mechanical testing[10], therefore, three test pieces will be required, namely, one for tension, one for impact, and one for compression. Bearing in mind the important nature of the figures for the tensile strength, two test pieces of different cross-section should be used. From manufacturing considerations, the best shapes for this purpose are short, compact 8-shaped solids, in one of which the smallest cross-section is about 2 sq. cm. and in the other about 10 sq. cms. These can be easily turned from a well wedged "leather hard" body and should be fired in a hanging position. By comparing the figures for the 2 and 10 sq. cms. pieces, a measure may be formed of the greater or less proportionality between strength and cross-section and, in this way, the mechanical quality of the product may be evaluated. In place of the usual rod-shaped dumb-bell used for tensile tests, a shorter form of the test piece is recommended for testing, since the latter form allows the tensile strength of the material to be determined in the most reliable manner. Genuine porcelains tested correctly in this manner give a tensile strength of about 320 to 340 kgs. per sq. cm., *i.e.*, about 40 per cent. higher than common porcelain. For impact testing, thin unglazed rods of about 2 cms. square cross-section, which have been fired in a hanging position, should be used and tested in the same manner as that employed for metals. In this test the values are higher the more the structure approaches that of genuine porcelain. The mean value of genuine porcelain is about 2 centimetre/kgms. per sq. cm. Finally, for the compression test a small cylinder of about 4 cms. diameter should be taken and tested in the usual manner in the hydraulic press between soft cushions made of copper foil. Although the figures for genuine porcelain under this test are high, other porcelains can be produced giving figures of equal magnitude or even of slightly higher value, since in non-genuine porcelains there are often large quantities of stony broken pieces, which lie close to each other and are united by the quartz felspar glass. Owing to their natural hardness, these pieces are better able to resist compressive stress than the homogeneous material of genuine porcelain. Results of this sort have, however, nothing to do with the nature of hard porcelain.

These test pieces, namely, the solid cylinder described above of from 6 to 8 centimetres diameter, a thin section made from it, a square unglazed porcelain plate of about 10×10 centimetres and 3 mm. thickness, two 8-shaped solid bodies made with cross-sections of 2 and 10 sq. cms. respectively, a round porcelain rod about 1 cm.

thick and a small solid cylinder of porcelain of about 4 cms. diameter, give complete information as to the quality of the material which a porcelain manufacturer proposes to employ for high tension electrical work; in the same way as steel manufacturers supply sample pieces for tests, or copper and brass works supply samples of their alloys for testing the material which they intend to use at a later date for their products. The production of test pieces of this kind is as simple as the testing itself and, what is more important, it is possible by obtaining such test pieces and the results of tests on them, to reach an understanding between the porcelain technical expert and the expert on high tension distribution in a much easier manner than by discussing the question as to whether a finished insulator has broken down owing to its faulty construction or because of bad material. The stipulations with regard to the supply of finished insulators, and all questions connected therewith, are not in any way limited or changed by these material tests. They are only amplified by the most important technical requirement, namely, that porcelain material must be as homogeneous as possible in its structure, that is to say, it must be genuiue.

There is a simple method of obtaining at least one indication of the quality of a hard porcelain. According to the views expressed above, it is clear that the quality of porcelain depends on whether there is more or less complete and uniform formation of sillimanite crystals in the porcelain body. Since sillimanite crystals enclosed in the silica felspar glass of the porcelain are much better able to resist the chemical action of hydrofluoric acid than the glass mass, in which they are embedded, the content of sillimanite crystals in the porcelain may be determined from the resistance of a piece of the porcelain body to the influence of hydro-

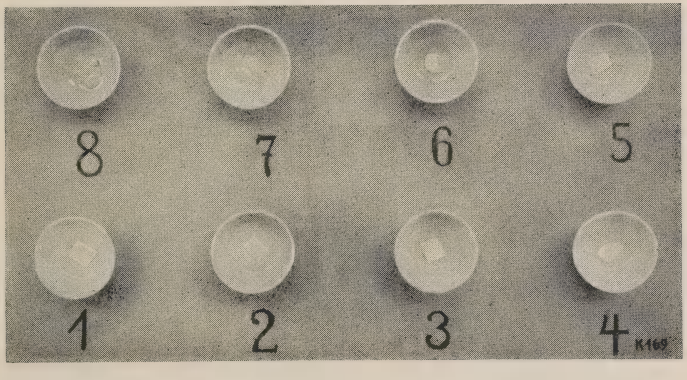

Fig. 7.

Resistance of various hard commercial porcelains to attack by 50 per cent. hydrofluoric acid.

fluoric acid. By means of this simple test, therefore, an approximate estimation may be formed of the value of the porcelain. Mineralogists have used a method of this type, depending on the variation in resistance to chemical agents, in order to isolate the individual components from clastic rocks. The most general practical application of this method is that discovered by Brongniart and developed by Seger for the rational analysis of ceramic raw materials. The result of a test of this sort on eight hard porcelains is shown in Fig. 7. From the porcelain material to be tested, small cubes with edges about 7 mm. long were cut out and these cubes were placed in porcelain dishes the insides of which had been covered with paraffin, and subjected to the action of 50 per cent. hydrofluoric acid for several days. In the first porcelain dish, the cube, which was composed of hard porcelain retained its shape and sharp outline unchanged, as can be seen from the photograph, owing to its high and uniformly distributed content of sillimanite, whilst all the other porcelain test pieces softened under this test or, as the last dish shows, owing to the complete absence of sillimanite crystals, were entirely dissolved by the action of the hydrofluroic acid.

A further method of obtaining information regarding the structure of a porcelain body, especially its content of free silica, is provided by the mineralogical microscope, preferably fitted with an arrangement described by Professor Dr. Köhler, of the Zeiss Works, Jena, for producing circularly polarised light.[11] In the circularly polarised light between crossed nicols, practically all the free silica particles contained in the thin section of the porcelain body appear more or less light against a dark background, and from the quantity, and above all from the character of these silica grains, or quite generally from the appearance of the field obtained in natural and in polarised light[12] by optical investigations of this character, very comprehensive conclusions may be reached as to the composition, the firing, and the properties to be expected from the finished porcelain. Optical investigations on porcelain of this character require years of experience and untiring experimental work, if the results obtained from them are not to be merely of a speculative nature.[13] With this proviso, however, optical methods form the safest guide for the examination and evaluation of porcelain.

High tension porcelain is a typical electrical insulating material and, as such, it must be able to withstand many sorts of stresses and disruptive influences, while remaining stable and homogeneous. The fact that the ability of electrical insulating material to withstand electrical stresses is not alone decisive in determining the value of the material for electrical purposes has long been appreciated in technical circles as far as other insulating materials are concerned, as, for instance, varnishes for electrical purposes. And the methods of judging the value of high tension porcelain will also undergo a

similar change in the future, when the knowledge of this material improves, and the electrical resistivity will be regarded more and more only as a subsidiary attribute of the material. The various specifications and methods of testing called for by electrical engineers, whether they are for 50 cycles A.C., high frequency or shock testing, deal principally with the shape of the material, which is assumed to have been manufactured correctly, and not with the material itself ; but already a change is taking place. Electrical engineers are beginning to pay more and more attention to the porcelain itself, *i.e.*, to the pure material, and are demanding that the secrecy and empiricism, which have hitherto characterised ceramic procedure, shall be abandoned in favour of scientific research and constructive work on the problem of silicate insulators. The difficulties of this work,[14] however, can only be appreciated by those who realise the complex, varied, and almost boundless nature of the task.

REFERENCES.

1. K. H. Reichau. "Contribution to the better knowledge of genuine hard Porcelain." TRANS., **23**, 145, 1924.

2. O. Boudouard. "Porcelaines électrotechniques." *Chimie et Industrie*, **6**, 584, 1921. La porcelaine constitue un système en equilibre instable, qui tend justement à la formation de sillimanite et d'un verre quartzeux.

3. A. B. Searle. "The Chemistry and Physics of Clays." London, 1924, page 17. States of Aggregation : "The ideal structure of glass pots, according to M. W. Travers, consists of a network of sillimanite crystals interwoven so as to form a strong and sufficiently dense mass. This is also the ideal structure of all refractory clay products, but it is never (!) attained on account of the long period of heating which would be necessary to convert all the clay into sillimanite." That is to say, all ceramic products could reach this ideal structure if they were only heated for a sufficient long time. This is not the case.

4. Ideal porcelain should consist of a mixture corresponding to the formula $Al_2O_3SiO_2$ (sillimanite) and a fusible glass which binds the other particles firmly together. When materials capable of producing such a mixture are heated to a sufficiently high temperature, they will form a felted mass of sillimanite needles bonded with a glassy cement. (A. B. Searle. "The Chemistry and Physics of Clays," London, 1924, page 375).

O. Boudouard. *Ibid.*, p. 583. "On admet généralement qu'une bonne porcelain est fonction de développement de la sillimanite ($SiO_2Al_2O_3$) et de la solution des grains de quartz dans la masse.
Also Eugenio Alessandri : "Composizione, Microstruttura e Proprietà dela Porcellana." L'Elettrotecnica Milano, **11**, page 285. La porcellana è un agglomerato di argilla e di quarzo cementato da una massa vetrificata proveniente della fusione di feldspato o di simile silicato fusible. La porcellana non (!) è trasparente ed è anisotropa.(!)
From a purely chemical standpoint, genuine porcelain represents, at the high temperature of the porcelain kiln, a saturated and homogeneous silicate dispersion, which is practically in labile equilibrium, and which, on cooling, tends asymptotically toward a stable equilibrium, the dispersiod phase, no longer capable of existence, changing to a crystalline silicoid. The whole process is entirely controlled by the law of mass action. The intensity and direction in which the

alumina and its silicate derivatives react by virtue of their amphoteric character, constitute a decisive factor in the whole process of porcelain formation in the kiln. This decision rests with the clay substance and takes place at a time when the other components have not yet come into operation. Accordingly, sillimanite represents only one of the possible crystalline forms in which the silicoid may separate out in the homogeneous quartz-felspar glass.

5. *cf.* A. B. Searle : "Chemistry of Physics of Clays." London., 1924, page 377. Fluxes in Porcelain. "The chief purpose of the clay and some of the free silica (?) in all porcelain is to produce the felted mass of sillimanite crystals, which form the skeleton of the finished ware, and to provide a reinforcement which will prevent (?) undue distortion of the ware." The free silica in a body does not assist, but rather prevents the formation of sillimanite as can easily be shown. For the formation of sillimanite, the clay substance and felspar contained in the body are alone responsible, the former in accordance with its geological formation and its capacity for dissociation, the latter according to the degree of saturation and alkalinity which it develops in the porcelain kiln. A body which, owing to its high content of silica, shows little tendency to the formation of low-silicate complexes, can actually be made to produce such complexes readily, including sillimanite, by the addition of small quantities of chemical reagents ; just as it is possible, by small chemical means, to prevent a body, which, otherwise shows a strong tendency toward dissociation in the porcelain kiln, from fully developing such tendency. Such means should, however, be employed with the greatest caution, in view of the possible effects upon the properties of the finished porcelain. The presence of free silica must always be regarded as responsible in a high degree for the "undue distortion of the ware."

cf. also. O. Boudouard, *Ibid*, p. 589. La fabrication d'une bonne porcelaine dépend de la formation des cristaux de sillimanite, et si tout le monde est d'accord sur l'existence de la sillimanite dans les porcelaines, il reste encore quelques obscurités sur les modes et conditions de formation de ce composé.

The above quotations demonstrate quite clearly how the introduction of natural sillimanite into ceramic bodies, as has been recommended frequently of late, is to be judged.

6. I am indebted to Prof. Köhler of the Zeiss Works, Jena, for these photographs. He has accorded me valuable assistance in the optical examination of ceramic products and I should like to take this opportunity of expressing to him my sincere thanks.

7. Eugenio Alessandri : "Composizione Microstruttura e Proprietà della Porcellana." *L'Elettrotecnica*, Milano, **11**, p. 289. Jo ho esaguito 150 sezioni sottilie microfototrafie di porzellane provenienti da numeros manifatture europee ed americane ; il quarzo cristallino remane ancora abbondante entro la massa di tutte e più che mai di quelle che hanno tra o loro tecnici chi sostiene che una buona porcellana di isolatori non deve contenere quarzo indisciolto.

La sillimanite (!) cristallizata in aghi ben definiti si osserva (in pochi campioni) soltanto nella zona di passagio (!) tra la vernice e la pasta.

8. F. Grunewald. Die Durchschlagsfestigkeit von festen, geschichteten Isoliermaterialen *Arch. für Elektrotechnik*, **12**, 79, 1923.

9. *cf.* H. G. Montgomery. *British Clayworker*, **33**, 114, 1924. "It is well known, that the effect of repeated firings is cumulative. It has been found that, no matter how high a temperature has been attained in a single firing, the quality of the material is not so good as that which has been fired repeatedly at a somewhat lower temperature."

These remarks refer to grog, but it is obvious from the context that they may also be applied to porcelain.

cf. also Frank H. Riddle. The Production of Porcelain for Electrical Insulation. *J. Am. Inst. Elect., Eng.*, p. 343, 1923. "For electrical purposes only the hard porcelain is used in Europe; however, the American product, although made at slightly lower temperatures than 1,400°, is considered superior."

And the continuation of the same paper on page 1,101: "The mechanical strength of a porcelain depends more upon the temperature to which it is burned than any other one thing. The higher temperatures produce the stronger bodies. It is evident form this, that the tendency among the manufacturers is going to be to increase their burning temperatures and increase the fineness of grinding of the body ingredients. This will mean a greater cost, but the quality of the ware will still warrant the increase." Riddle therefore desires the raw body to be ground more finely and then fired above 1,400°, as is done in European hard porcelain practice in order to get better porcelain. Then, however, in accordance with his statement on page 343, his porcelain will become just as bad as the European hard porcelain.

10. R. Rieke and M. Gary. Die Prüfung von Porzellan. *Ber. deut. ker. Ges.* **3,** 5, 1922.

11. K. H. Reichau. "Contribution to the Better Knowledge of Genuine Hard Porcelain." TRANS., **23,** 145, 1924.

12. For my optical tests I used the minerological stands of the firm Zeiss-Winkel, including the large stand V1.M. with Ahrens' prism and fluoride system. The optical equipment of these stands is unique and unsurpassed for this type of investigation. The firm Voigt and Hochgesang, of Göttingen, has prepared hundreds of thin sections of ceramic products for me in masterly perfection, down to sections 0·01 mm. and less.

13. A paper by A. A. Klein is characteristic: "Constitution and Microstructure of Porcelain." Bureau of Standards. Technologic Papers **11.**, 80, Washington, 1916. On page 34 of this paper is the following sentence: "If there were great differences in constitution caused by small differences in duration of burning, a low temperature body burned for a longer period would resemble a high temperature body burned for a shorter period. Fortunately, this is not the case." As the above remarks have shown it is possible to hold quite a different opinion.

From the micro-photographs and thin sections prepared by H. A. Brady for Mr. Klein, far reaching conclusions may be drawn if the photographs are properly interpreted; these consclusions are much more valuable than those which Mr. Klein has drawn.

cf. also H. G. Tufty, "Photographic Study of Porcelain Insulators." Research Dept. University of Wisconsin. *Electrical World*, **73,** 268, 1919. As the result of his study of a number of American insulators, Tufty finds "three very noticeable points. The first is that the quartz is unaffected by any firing temperature and remains practically constant. The second noticeable point is, that the porosity of all the sections was very low. The third point is, that there is an absolute lack of any crystals other than the quartz." These results are scarcely calculated to support the superiority of the American porcelain insulators over the European product, as claimed by Riddle.

14. *cf.* G. N. White. "The Manufacture of English Chemical Porcelain.', *Chemical Age*, **9,** 334, 1923. "Since the manufacture of porcelain involves the re-actions of the complex silicates, it is usually regarded by chemists as incapable of receiving direct scientific treatment. Nevertheless the pottery industry possesses problems in urgent need of solution." *Cf.* also preface to A. B. Searle, "Physics and Chemistry of Clays," London, 1924.

XXV.—Pin-Holes; and Some Other Things.

By H. J. Plant.

COMMENTING on pin holed ware some years since, an expert wrote: "It is perfectly obvious that there is more than one cause at work," and anyone who investigates this subject for some time will come to the same conclusion.

Pin holes may be divided into two classes: (1) Body Pin Holes; (2) Glaze Pin Holes.

It is believed that the former predominate, but to find out the actual cause, careful observation is necessary, and the object of this paper is to assemble, in simple form, as far as possible, various opinions and facts on the subject.

It is certain that great loss is caused by this fault. In one case, a manufacturer estimated that his loss, through this cause alone, amounted to £2,000 in a period of about twelve months, and from time to time one is asked the question: "What can we do to stop pin holes ?". It is very difficult to give an answer at once, because so many things contribute and assist in the development of this fault. It occurs under the most peculiar conditions, and each case needs separate and close investigation.

Some time ago we had an exceptional quantity of pin holes which occurred principally in a certain shaped cup, and, peculiarly enough, on the plain shapes that were thrown and turned the pin holes did not occur to any extent. In this shape, however, although it was a thrown shape, the turning was reduced to a minimum, and pin holes developed all round the handle. The increase here was due to the sponging necessary in finishing the handle, thus distributing the surface of the clay, and revealing the pinholes. The fault, however, was deeper than on the surface, for samples were ground on the polishing lathe until the pin holes were found deeply embedded in the body itself, thus demonstrating that the fault was due to bad clay preparation.

In three samples of china, made by a Longton manufacturer, great care had been taken to examine personally and mark the pin holes on the surface in these particular pieces that were visible in biscuit, yet, after the ware was glazed and fired, the pin holes originally marked disappeared to some extent and fresh pin holes occurred, of which there had previously been no trace. One can safely assume, therefore, that there are two types of pin-holes, one due to air or gas bubbles in the clay (these were visible in the biscuit pieces), and the other due, in all probability, to plaster taken from the moulds, and later on dissolved in the glaze.

We therefore find that the first essential is a body free from air bubbles, and one must start right at the beginning, taking:—(1) The Materials; (2) The Mixing; (3) and finally, the Pugging.

As far as materials are concerned, there is not much to trouble an earthenware manufacturer, unless he happens to use materials that are dried on the kiln, and is unfortunate enough to receive a supply that has been burned in the drying process. This in itself would be likely to give rise to trouble and loss. The china manufacturer, however, who is tempted by the low price to use large quantities of soft calcined bone, would probably suffer from an epidemic of this trouble. A body made of this material will be most unsatisfactory.

BONE.

The quality of bone used affects this question of pin holes in no insignificant way.

It has already been shown that inferior bone is a prime cause of trouble, but however good the bone is, care must be given to its proper calcination. Some manufacturers believe in calcining so thoroughly, that practically no black, or partly calcined matter, is left in it. I believe, myself, that where the bone used is raw bone, more or less in its original condition except for the fact that it has been de-greased, thorough calcination is very satisfactory in all respects, but where the bone used is largely digester bone, that is, bone that has been chemically treated to extract all its fats, it is necessary, on calcining, to leave in a certain amount of black undercalcined pieces, the reason being that bone containing a proportion, say about 10 per cent. of this undercalcined material, has a tendency to make the body more plastic than it would otherwise be. It would appear that some chemical change takes place in the ark, giving to the resultant mixture that soapy feeling which we potters so much desire.

The question arises, therefore, "How are we to get rid of the resultant gases set up by this chemical action?" because these gases mean bubbles, and unless controlled, ultimate pin holes. The answer to this question is: "Ageing in the arks before use in the final mixing." Then again, it is important that bone should be finely and uniformly ground, and it should be given a thorough washing in the mill, so as to free it from coarsely ground particles.

The drying of ground bone should be done in such a way as to avoid boiling, yet, at the same time, there should be a steady evolution of moisture, so as to prevent the surface of the bone skinning over, and thus tending to prevent the dissipation of the innumerable minute blibs that are always present in water-ground bone.

Bone should never, on any account, be overdried. A manufacturer may insist on having materials delivered in a dry state from the mill, with the idea that he is getting better value for his

money, but the losses in making more than counteract the possible saving through buying dry bone.

It is always as well to dry bone as far away from the fire-mouths as is possible, and in one modern mill at least, having drying kilns 20 to 30 yards long, the fire has to travel along 12 yards of flue before it comes to the section used for bone drying. The result from this particular mill, therefore, is uniform and satisfactory. About 12 per cent. of moisture in the bone is a correct standard to aim at. Then again, unless the slop bone is aged, in order to give it time to rid itself of any gases which may be formed, its use will still be a source of trouble.

BLUNGER.

It is in the slip house that most of our trouble as regards body pin holes has its origin. Clay must be blunged properly, sufficient material should be in the blunger to cover the whole of the knives, the object of this being to rid the clay of any air bubbles rather than to encourage them. The blunging should be carried on until the whole of the material has been reduced to a creamy consistency, free from lumps of any sort, other than the small amount of coarse matter that would be contained in the ball clay, if this material enters into the composition of the body.

A manufacturing friend of mine suggests as a cause, that slip-makers, in an endeavour to increase their output, rush the blunging, and thus try to make the sifters do the work that the blunger should do; but this most assuredly leads to blibbing clay and slip, to say nothing of other faults that may develop from the same cause. Possibly manufacturers may have noticed how their losses increase as soon as extra pressure of work means a general speeding up, and some of this loss, undoubtedly, commences in the slip house.

SLIP PUMP.

After the slip is blunged and sifted, it is desirable to see that the pump is in perfect working order, so that slip only, and not slip mixed with air, is pumped into the press.

PRESS CLOTHS.

Press Cloths themselves are sometimes responsible for pin holes. The preparation used for preserving these cloths often helps to spoil an otherwise good mixture. We believe that the new green cloths, with which most of us are familiar, are a distinct advance on the old ones.

STORAGE.

It is obvious in connection with these remarks that the proper storage of clay, before pugging, is essential, if the best results are to be obtained. The atmosphere should not be too dry, and the place as free from draughts as possible. The clay should be

"mawed" (mauled) as it is removed from the clay press, and covered until required with sheets kept in a damp condition.

PUG.

The pug has been found to be a prime cause of pin holes in the china body. Good pugging is absolutely essential if loss in this direction is to be avoided. No attempt must be made to pug clay that is too soft when it comes from the press. Watering the pug must be absolutely forbidden. Soft and hard clay passed into the pug together will never mix properly, the reason being that soft clay tends to stick to the knives and barrel of the pug, and renders it impossible for it to become properly compressed so as to eliminate air bubbles. It has been found in practice that one knife too many, or one knife too few, has been the cause of faulty clay, and one can readily believe that, if the angle of the knives is not correct, it will be impossible to get the solid result which is necessary.

Having thus produced clay and slip under the most favourable conditions, we have now to safeguard their use so as to produce ware free from pin holes.

Slip for casting should not be used straight from the slip house, but should be stored in the shop in which it is used for as long as possible, so as to avoid too great a variation between the temperature of the slip and the temperature of the mould. Great benefit has been derived by dabbing the moulds, before pouring in the slip, with slip that has been previously stored in the stove itself. The moulds should not be used hot from the stove, but should be allowed to cool somewhat.

PRESSED AND JOLLIED WARE.

There is no doubt that the same precaution with regard to hot moulds should be taken in the case of pressed or jollied ware. The elimination of pin holes in flat ware and saucers has been brought about successfully, in some cases, by the installation of a fan, thus making possible the towing and dry fettling of the ware, instead of the more usual sponging. This process, of course, is common in earthenware, but is not so common in china. There is, however, not the least doubt that it proves to be the greatest help, and is very often a complete cure for pin holes in flat ware.

ALKALINE SLIP.

In the case of cast ware, made from alkaline slip, in addition to some of the causes previously mentioned, the introduction of dry scraps added to the mixing is likely to introduce this fault, as the air, entering the pores of the clay, has little opportunity for escape, owing to the slimy condition the slip attains when alkalies are introduced. If moulds are very wet, or dry, the same fault arises, and it is advisable in the case of very dry moulds to sponge the face with clean water before pouring in the slip. Pin holes in this case are probably caused by the displacement of air

in the pores of the moulds, for, as the moisture in the slip is absorbed by the moulds, some of this air enters the mixture. If moulds are filled too rapidly, pin holes are introduced; also if the moulds are filled from taps when the slip is under too great a pressure; or if the slip, when kept in a state of agitation, is agitated too rapidly, so as to develop air bubbles instead of causing them to escape. Needless to say, all slip should finally be sieved before being passed out into the moulds.

Local pin holes may be caused by the use of excess water by the potter when working the clay—for instance, when making the lip of a ewer, or even when fettling a handle.

DUST.

It has been found that dust plays a large part in the creation of pin holes, but these are not body pin holes in the sense mentioned in the previous remarks. The dust factor may be divided into various groups: (*a*) dusty moulds; (*b*) perished moulds; (*c*) dust on the biscuit ware.

Some loss is caused in this direction by the use of moulds that are too old. The surface plaster, being in a perished condition, is taken up by the clay during the making process, and in a later stage of firing this either fires out or dissolves in the glaze, and pin holes of a very serious character are the result. It is difficult to trace occasions in which pin holes are due to dusty moulds, but not so difficult when due to perished moulds.

A prominent local manufacturer of electrical goods, troubled very much with pin holes, found that the cause, which it was very difficult to trace, was due to dust on the biscuit ware, and it was entirely removed by washing the ware before dipping. We have personally applied this remedy in the case of china, but as far as we can see it does not apply here. There is no doubt, however, that dust in certain cases on the biscuit ware is a prime cause of this fault.

The experience referred to previously, of a manufacturer who lost very heavily in one year, may interest you. He was making a fine line of underglaze hand-painted pottery. A palette of colours had been specially made, good business resulted, and very successful results obtained, when suddenly, without any warning, pin holes developed on the surface of the finished ware. This resulted in a very large percentage of seconds—50 per cent. at least of the goods coming from the ovens being faulty. Immediately steps were taken to trace the cause. The body was carefully examined, special precautions taken in the slip house, the glaze was brought under suspicion, and experiments made with other glazes, but the improvement was practically nil. Then came a long series of experiments with the colours; some improvement was effected by fluxing them, but still the loss continued, until it became almost impossible for the works to

deal with the orders on hand. Months had meanwhile passed in this effort to trace the cause of the trouble, and as often happens, the remedy was the simplest possible. Instructions were given that all the biscuit ware, before decorating, was to be washed in clean water. Immediately the pin holes disappeared, and up to date there has been no further trouble in this direction. It will be seen, therefore, that dust on the surface of the ware may be a prime cause of pin holes, and it may be laid down as a fact that it contributes in a large degree to body pin holes also.

FIRING.

Even now the whole of the ground is not covered. Firing may have quite a lot to do with this fault. It has been found by experience, that with some types of ware, and under certain conditions, rushing biscuit ovens during the first 12 to 18 hours firing has been a specific cause. One manufacturer at least lights his china biscuit oven at 8 o'clock at night, and leaves it unattended, doors and dampers open, until the next morning. He states that, as far as he is concerned, pin holes are practically unknown.

GLAZE.

A faulty glaze mixture may result in an apparent increase in pin holes, owing to the fact that it may be so viscous that any tendency to pin holes in the body would be revealed.

I will conclude with a summary of pin hole causes:—(*a*) The preparation of material or clay may be at fault; (*b*) Imperfect blunging; (*c*) Insufficient ageing; (*d*) Faulty pump, pumping air instead of clay; (*e*) Bad Pugging; (*f*) Press cloths; (*g*) Dust on the moulds; (*h*) Perished moulds; (*i*) Too much water used by Potter; (*j*) Cast moulds, too wet, too dry, or too hot; (*k*) Bad firing; (*l*) Faulty glaze mixture.

SOME OTHER THINGS.

I believe that, in spite of all the discoveries in the past, the possibilities of improvements are still very great.

GLAZES.

Many of the glazes, for instance, in use in this district, are based on old formulæ built up by the practical rather than the scientific mind, and here I wish to develop a theory with regard to glazes that may be of some general interest.

In the TRANSACTIONS (**13**, 30, 1914), Dr. Mellor gives a paper on the behaviour of some glazes in the glost oven, and Point 5 refers to rolling and crawling of the glaze.

There is close relationship here, I believe, between that and the frizzling or crawling of transfers. It is a well known fact among certain manufacturers of transfers, although not generally known to the manufacturers of this district, that when making

transfers, if more than one colour is superimposed, the soft colour must, wherever possible, be printed last, and the colours arranged in such a way that, when transferred to the ware, the low-melting colour is in contact with the glaze. In this way it adheres firmly and never becomes detached from the glazes. Transfers made on this system will not frizzle or crawl, and those of us who have suffered from this trouble may well be glad that a way out has been found. If the reverse procedure is adopted, (the hard colour coming next to the glaze, the soft colour on the top), the soft colour commences to fuse, curls over, and ultimately pulls the hard colour with it.

Something of this kind may readily take place in a glaze where the mixture is faulty.

First of all I would like to say that a glaze suitable for china and earthenware, which will not run off the edges, *i.e.*, a hard glaze, and which will not scratch easily, or stilt-mark, is probably the worst type of glaze for covering pin holes, assuming always that this glaze is made on the old lines, with one frit having a standard melting point.

The suggestion I make is as follows:—Two frits should be made in addition to the lead frit—the first frit, which forms the bulk being very hard, and the second a very soft borax frit. The fusible frit will act as the covering agent, and will grip the ware early. It is difficult to demonstrate that this is a fact, but it has been proved beyond doubt that, if a hard frit is ground up fine and scattered over the surface of a piece of buscuit ware, it will fire at certain temperatures into small globules; but if the mixture used be separated into two frits, one a very soft one, the result will be a covering of the surface. Why this should be so is difficult to explain, except that the soft fusible mixture gets a grip of the surface at a lower temperature, and ultimately unites with the harder.

Underglaze Colours.

Though it may not be a well known fact, in the case of underglaze colours, much loss has been caused through curling away from the ware. Underglaze brown is particularly liable to this fault, but it can be readily overcome by adding 1 oz. of No. 8 flux to 5 or 6 ozs. of colour. Here again the flux grips at a very low temperature, long before the glaze has started to melt, and the trouble has been absolutely overcome. But it must not be taken for granted that this quantity applies to other colours as well as brown.

Bone China Body.

For some time I have held the theory that the ideal bone china body should be practically vitreous in the biscuit state, yet nowhere have I been able to find a china body in bulk which will not absorb ink. Dozens of different makes, including some of the

more famous, have been tested; yet only individual pieces here and there have satisfied the conditions which I have presumed to lay down as ideal. If an individual piece can be right, it is not saying too much that the whole may be right, and this, I suggest, is a subject for interesting investigation.

I have pleasure in submitting what, I believe, very nearly approaches the ideal earthenware body.* It can be decorated in a manner exactly similar to that used for china ware without fear of spitting-out or crazing. The body is delightful to handle from a potting standpoint; the biscuit ware has quite a satin-like surface.

This earthenware body costs less, yet is far stronger, and more durable, than the general type of earthenware made to-day. The loss from the ovens is reduced to a minimum, and, apparently, it will not craze, spit-out, or peel, under any reasonable conditions. In addition to this, it dips so easily that there is practically no need for a drying mangle.

It may be possible, and we believe it is, to make a china body that will be highly resistant to fracture. Investigations on the lines previously mentioned with regard to porosity will, I feel firmly convinced, produce this desirable result.

Ordinary practical experience may enable a potter to arrive at these ideals somehow or someday, but, generally speaking, one needs chemical knowledge, sensibly applied to problems such as these, to enable one to attain the desired result.

* Samples of this ware were submitted for inspection.

XXVI.—Notes on Grinding and Crushing Machinery.

By F. Lane.

THE raw materials used in the metallurgical and in the clay and allied industries usually receive a preliminary treatment in some form of reducing machine, which reduces the product, in one operation or by stages, to the required fineness. The suitability of the machine to be used is determined by actual inspection of the material; its hardness, tenacity, greasiness, adhesiveness and structure; the natural state, the moisture content; the available size as delivered to the machine, and the output required in terms of quantity per hour and fineness of reduction. The question of class and degree of sizing of the product treated should be definitely known and decided before the machinery is selected, since definite rules, tables and formulæ are helpful only in focussing the mind. Materials vary so much, and the manufacturing requirements differ to such an extent, that each individual case under consideration stands somewhat isolated, to be tackled best by ingenuity and experience. Still, the following notes hold good in the reduction of any materials treated under this title:—

(*a*) Get rid, as they are made, of reduced sizes in order to bring surfaces of the material to the action of the machine;
(*b*) Arrange your feed in regular and sufficient quantities to suit the output of your machine;
(*c*) Limit the size of the largest pieces fed to the machine;
(*d*) Limit the water content of the feed;
(*e*) Keep a clear discharge.

Simplicity in the design of the plant is a necessity. On account of power lost, both in the machine and in the material treated, the efficiency of crushing and grinding plant is comparatively low. The sources of loss appear in (*a*) wear and tear of the machine parts exposed to the work; (*b*) heat produced in the machine, the material and the atmosphere in contact with the work; (*c*) useless production of dust.

In selecting the type of machine, it should be borne in mind that, since ores, rock, and clay are weakest in tension, it is more economical to break than to crush, and to crush than to grind. This will determine the class sequence of machines used in the reduction, and will divide the subject into the following heads:—breaking, crushing, grinding, pulverising, breaking being the preliminary stage; crushing the primary stage; grinding the secondary stage; and pulverising the final stage. The stages required are determined by the structure of the material and the final size required.

Reducing by Breakers.

Breaking is effected by "pressure and release" alternating machines acting on commercially dry material. Breakers are of three types: (1) the reciprocating, or jaw breaker type; (2) gyratory or conical breakers; (3) revolving or disc breakers. In the reciprocating type, the material is broken between a fixed and moving jaw as the latter advances towards the former. The discharge of the broken material is effected on the succeeding retirement, this disposition of the jaws allowing a further feed of fresh material to be broken. The standard machines of this class are of the Blake crusher type, built by the leading crushing-machine makers, with their own modifications in design (see Figs. 1, 2, 3 and 4). In

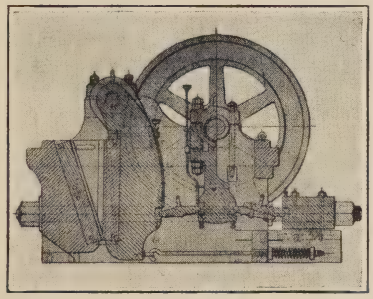

Fig. 1.

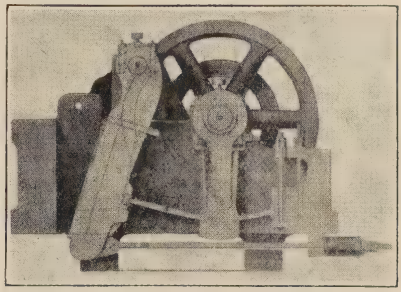

Fig. 2.

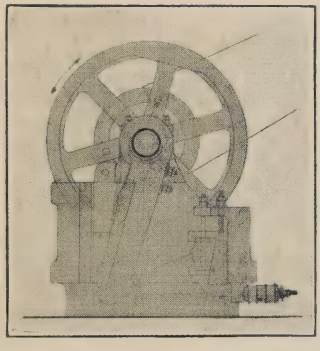

Fig. 3.

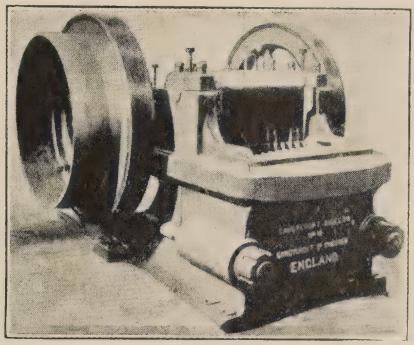

Fig. 4.

these machines the reciprocating jaw operates within a heavy iron or steel frame, having the fixed jaw held vertically at the one end, and the bearings suitably placed supporting the moving jaw, which hangs at an angle of about 20° toward the fixed jaw. In the opening

thus formed we get at the top the greater width termed the mouth; the smaller opening at the bottom is the discharge, and the intervening space is called the throat. Midway between the swing jaw and the back end of the machine body is the "Pitman," which hangs vertically on an eccentric shaft and is connected in suitable seats by a toggle link, to the back of the machine and by a similar method to the swing jaw. At each revolution of the eccentric shaft, the Pitman rises, and the links cause the swing jaw to advance. When this advance is complete and the Pitman descends, the swing jaw is pulled back by a tension rod actuated by a steel spring (Fig. 1) or stout rubber buffer (Fig. 2), its own weight helping. Broken material is then discharged, and fresh material slips down the throat. The eccentric shaft carries the driving pulley and becomes the driving shaft, making 150/250 R.P.M. in the larger machines, and 250/450 in the smaller machines. Uniformity of effort is maintained by two heavy fly wheels, one at each end of the shaft, which absorb energy during the retirement stroke to give it out on the advance stroke. The speed of the crusher is relative to the hardness of the material to be broken, high speeds being more effective for hard stone.

The size of material which a machine will take, and the size reduction which it will effect depends upon the dimensions of the two jaws and their disposition to one another. These two factors are stated in terms of dimension from side to side of the machine, and distance from jaw to jaw, the ratio of the former to the latter being $1\frac{1}{2}:2$. The depth of crushing throat is most important, and is, with the ordinary angle of 15° to 20°, usually from 2 to $2\frac{1}{2}$ times the width of the mouth (See Figs. 1 and 2). Variations from 15° to a greater angle between the jaws are allowable, and indeed are necessary, according to the class of material, as it affects the desired size-ration of material crushed, and given output. In many machines the angle varies on the face of the swing jaw, the mouth and upper throat having a lower angle, and the bottom throat a larger angle; this prevents choking and "scaffolding" of the feed, and gives less slip of the material. The wear plates of the fixed and moving jaws are corrugated in order to give a beam action to the jaws, which requires less effort and produces less fines. The breaking is done only on the advance of the swing jaw, and it is this intermittent action which render necessary the heavy fly wheels. This alternating of effort and rest gives concentrated action and necessitates ample strength in the machine to withstand the peak loaded stresses developed, which are further accentuated if the foundations are light or faulty.

The jaw breaker is simple, reliable, and takes up little space. It should be placed in an accessible position, so that replacement of parts can readily be made by mechanical aids; the position should be such that the feed may be continuous and of the required quantity; the discharge should be free, with easy delivery to the

elevator or screen or machine into which it is intended to feed. Most of the wear on this type of machine occurs at definite points. The wearing parts are, therefore, made relatively small and reversible, faces and seatings having their surfaces cushioned on softer metal. Worn jaw faces reduce output in quantity and quality, and absorb more power, since the faces exert a purely compressive effort instead of the breaking effect of the beam action. Rock and similar materials are weak against tensile stress, and strong against compression. Systematic overhauling is necessary to ensure adjustment of worn plates where the size of the product is important.

In no case is the product of the jaw breaker very regular, especially when the materials are of a flaky nature. The output is more regular in size when the machine is fed fully loaded, not choked or overloaded. The hard nature of the work performed by these machines demands perfect design in lubrication, and careful application to prevent undue wear and loss of power. Jaw breakers of the Dodge type (Fig. 5) are really inverted Blake ma-

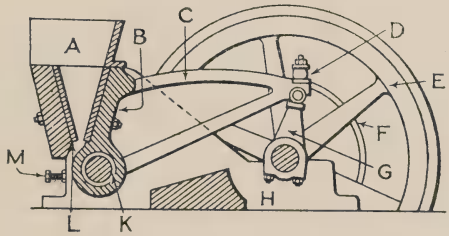

Fig. 5. Dodge Breaker.

A. Feed.
B. Movable jaw pedestal.
C. Bell lever.
D. Rubber buffer.
E. Flywheel.
F. Driving pulley.
G. Connecting rod.
H. Frame.
K. Shims.
L. Discharge.
M. Set screw.

chines, but in action they are not so efficient in output or so economical in consumption of power. It may be claimed that the product is slightly more regular in size than that from the hanging swing jaw type. Like the Blake machine, the principal parts are contained within a heavy rectangular frame, but the swing jaw is supported on a pivot shaft fixed below the discharge, while the connecting rod, instead of being a central vertical member hanging from the pivotal or ecentric shaft, is at the back end of the frame and sits on that shaft, its motion being transmitted to the jaw by a heavy bell crank lever of which the jaw is the short arm. Link plates or toggles are absent. The eccentric shaft is the driving shaft, and the intermittent action of the machine is balanced by two heavy fly wheels when compared with the Blake type. This inversion of details of the principal parts gives the swing jaw the

greatest movement at the mouth and the least movement at the discharge; hence the product will be more regular in the larger sizes; but, lacking freedom at the discharge, the machine is more easily choked. The moving parts are unwieldy, and out of balance relative to the output; thus the size and usefulness of the machine is limited. It cannot, therefore, be so universally used as the Blake type. Its most useful sphere is in dealing with the product from the latter type or a gyratory crusher as an intermediate unit. It may also be usefully used for preparing material for mills of the Huntington and Hardinge conical types, when not dealing with adhesive material such as talc or clay.

In all crushers of the Blake class, the heavy duty machines have solid cast steel (see Figs. 1 and 2) or built up mild steel frames (see Fig. 4), making for long life, and resisting the huge stresses set up without movement. Some makers produce crusher frames made up of thick mild steel plate, but my experience is, that these bodies "breathe" in the advance and retarding strokes, and lose some of their breaking power value, and injure the bearings and journals, and absorb more power.

Tramp iron is the great enemy of the stone breakers, and has brought many safety devices into being. Among them are toggle plates which are shaped to brake before other and more costly parts, or are made in two parts, with a rivetted overlap joint, in which the rivet shears when excessive pressure is exerted. Many favour a friction clutch at the pulley or on the line of shafting, which will slip when the power required to drive the machine exceeds a predetermined standard.

Gyratory Breakers.

The Gyratory Breaker (see Fig. 6) gives a continuous discharge of a fairly uniform size of material cubical in shape. The breaking is performed by the gyratory of a conical head within a fixed inverted conical ring. The head can be considered as the moving jaw, and the concave ring as the fixed jaw, of the Blake type. The machine is fed at the top, the broken material being discharged through a collecting spout set at an angle of 45-in. from back to front and enclosing the shaft. The body carries the inverted conical throat formed of renewable cast steel concave plates where the breaking is done. Immediately above is a ring which acts as a hopper to receive the incoming material, and to which are fixed three arms; the latter meet and form the hub carrying the upper end of the shaft, on which the conical head is fixed. The base of the machine supports the eccentric journal, the bevel wheel gearing, and the driving shaft. The path of the crushing head is both circular and rolling. This gyratory movement, approaching successively every point of the interior of the throat, gives a continuous breaking action, and is brought about by the eccentric journal causing the

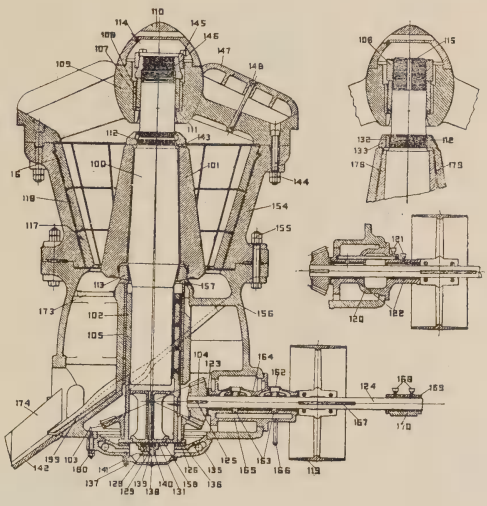

Fig. 6.

lower end of central shaft to move in a circle; the upper end in the spider arms revolves about a fixed centre, the bearing being free to take the inclined axis of the spindle. The sleeve carrying the bevel wheel is bored off centre to fit the crushing shaft, and is connected to it by a key. The driving shaft is supported in a long bearing fixed to the base of the machine, and carries the bevel pinion and the driving pulley. The adjustments necessary for sizing and wear are made within small limits by raising the spindle carrying the crushing head; or, if a larger difference is required, a thicker set of concaves is inserted.

A large portion of the work done by the conical head is taken, in the older type of machine, by the foot of the vertical shaft. This is a source of great resistance and loss of power. In the later type, the McCully (Fig. 6), this pressure is taken by the collar in the head of the machine, with more efficient results in work. The side pressure takes place at about the middle of the length of the shaft, and at all points in its circumference, at each revolution; severe bending action and fatigue are met by constructing this part of ample dimensions.

Compared with the jaw-breaker the gyratory machines employ power more efficiently, are less liable to scaffold and choke, deliver a more regular product, and are lighter in weight for a given capacity. The output is about 1·2 tons per H.P. hour. To overcome their main drawback, the height has been reduced by the introduction of a fixed central shaft. The Tilsmith breaker (Fig. 7) is typical of this class, and is 30 to 40 per cent. less in height than the Gates machine. The action of the conical head differs in

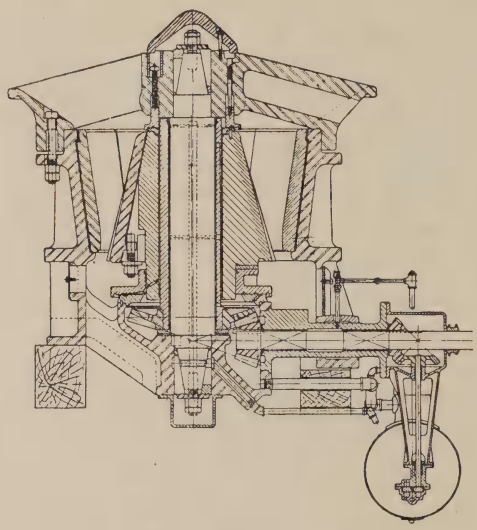

Fig. 7. Telsmith Primary Crusher.

that the crushing stroke is parallel to the eccentric, which is practically the length of the shaft acting directly on the head, causing a uniform horizontal movement throughout the crushing space. Adjustment is provided for by a shank carried by, and fitting in, the cone, and attached to the adjustment plate by a sliding key. Set pins with nuts, placed round the shank, give the necessary rise or fall of the crushing head, for making the discharge larger or smaller, as the sizing conditions may require.

The conditons governing the use of jaw-breakers and gyratories are determined by the following conditions: Where the material is necessarily made up of large pieces, or of relatively small pieces for a given output, the jaw breaker will deal with the material more economically, as the size of a gyratory machine necessary to deal with such would be out of proportion to the required output; and with a relatively small feed, the possibility of the head giving a beam action to the material is so reduced, that it amounts to crushing by pure compression, for which this breaker is unsuitable. The physical properties of the material is a factor that must not be lost sight of. Rock that breaks into slabs or flakes gives a very irregular product in a jaw breaker, while a softer, adhesive body would choke up a gyratory machine.

The repairs to a gyratory breaker are greater and more complicated than in a jaw breaker, but the working attention and power required are smaller.

Dry Grinding by Edge Runner Mills.

(See Figs. 8, 9, 10 and 11).

Edge Runner Mills usually consist of two heavy rollers or runners revolving and traversing a circular path, on which the material to be dealt with is reduced. This path may be solid or perforated, and may be stationary or revolving, and is carried by an iron pan, circular in plan, with sides formed to retain the material being ground. The reducing action by crushing and shearing, is continuous, a wider roller increasing the shearing action. Motion is given to the pan, or to the runners, in case of a stationary pan, through bevel gear wheels carried by the framework and placed above them, in the majority of cases. The under drive type has the gear wheels arranged underneath the pan,

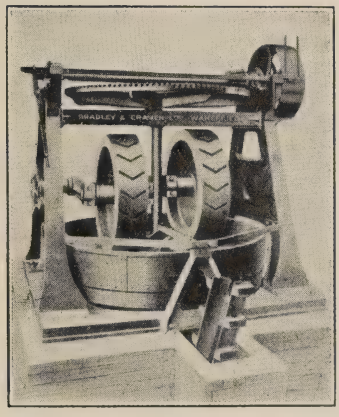

Fig. 8.

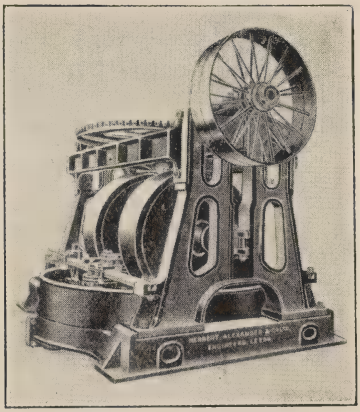

Fig. 9.

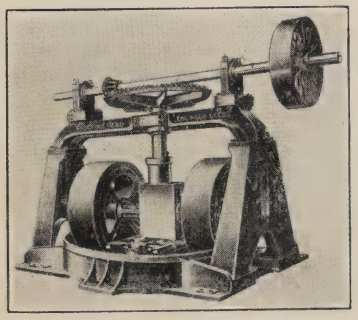

Fig. 10.

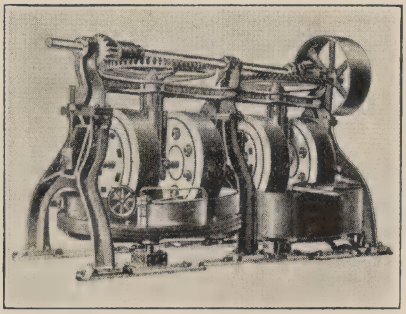

Fig. 11.

where they run in an atmosphere laden with dust and are difficult to replace in case of repair. An advantage here is that the power given to the gear helps to balance the total weight on the footstep. The edge runner mill should have an open base delivering on to the elevators conveying the ground product to the screens, thus obviating the work that would be absorbed by under-scrapers. This space should be built in water-tight concrete or brickwork, having sides of not less than 40 degrees and lined with hard cast iron segments to assist in preventing adhesion of ground material, and in cleaning when the mill is used for two or more bodies to be ground alternately.

The path of the runners, or the wearing plate, should be of hard cast iron, not perforated, save in exceptional cases. It should be cast in segments well bedded and bolted down to the pan body, and should be at least 4 inches wider than the runners, the upper face being in the same plane as the removable grids which occupy the space between the path and the outer rim of the pan. The grids rest on, and are secured by, bolts to rebated arms, and form the preliminary screening of the ground material, which is forced through them by plough or grinding scrapers, placed at a convenient angle, which will tend to arrest and distribute it across their face.

The holes in the grids are either circular or elongated, the shape being determined by the nature of the material ground. In all cases there should be taper from the face to give freedom of delivery, and this should be replaced when the perforations have become enlarged by wear. The proportion of grid area should be at least 50 per cent. of the effective pan area. The fact must not be overlooked that most materials to be treated are cohesive, and the grinding tends to compress lumps of ground material which can be separated by impact. This can be assisted by the revolutions of the pan being not less than 20, or exceeding 25 per minute, for diameters of 9 to 10 feet. It is a fallacy to economise on screens to the detriment of output, by the grinding mill doing its work more than once. The scraper or guide ploughs are supported by suitably placed bars, close to the frame work, and carrying adjustable fittings. The upkeep of the ploughs should be well attended to, and they should be designed to be reversible, or to have welded or replaceable wearing surfaces. The inside of the pan rim has much local wear from the material working between it and the ploughs, and should be lined for easy and cheap replacement. The runners should be of suitable weight and diameter, and the renewable rims as light as strength will permit, so as to make replacement economical. The tendency to use hollow rims seems extraordinary, since the efficiency of the mill as an effective grinder decreases in direct proportion as the concavity of the roll increases. This also applies to the roller path, or pan wearing plate. The rims

are secured to the roller bodies by bushes and bolts (see Fig. 11), or by staking wedges in wood and sometimes iron. The wood filling is assisted by iron counter wedges forming an effective connector which allows for easy replacement, and withstands the excessive vibration. The bushes of the runners must have renewable long bearings, lubricated with Stauffer greasers, and provided with loose collars between the stationary securing collars at each end. The runner shafts should be of ample dimensions, well secured to the central supporting collar that encircles the main shaft of the pan, and placed parallel to, but on either side of, the main diameter of the mill, in order to accentuate the shearing action of the runners. The outer ends of these shafts are secured to slide blocks having convex shoulders, and moving vertically in the housings of the mill. To prevent shock, arrangements by various makers provide for travel of the arms, and prevent the path and the rims of the rollers coming into actual contact. This distance also is regulated to the fineness of the grinding required.

In cases where it is inconvenient or undesirable to have an open base to the mill, a cast iron collecting pan is arranged immediately under the grids, having a suitable delivery opening and chute to the elevators: the material falling through is swept to this outlet by ploughs fixed to the arms of the revolving pan, or to the central shaft when the pan is stationary. It is advisable to have an inspection door suitably fitted in the bottom of the collecting pan, for purposes of renewing the scraper ploughs, and the securing bolts of the grids. Edge Runner Mills find almost universal favour in the clay industry, to the exclusion of practically all other types, showing an incredible amount of purely "follow the leader" methods used in a great and important industry. Grinding by edge runner mills requires little attention, and a minimum amount of repairs and replacement, which can be carried out by ordinary labour supervised by any intelligent mechanic. These good and simple attainments of this convenient type of size-reducing machines blind many to their useful applications. They are treated badly in all senses of the word. More often than not, they are irregularly fed, supervised by indifferent oversight, neglected in upkeep, and as long as they turn round are expected to turn out the goods required. The cumbrous mill, with its few revolutions per minute, has given place to the fussy high-speed revolving mill, light in construction, heavy in upkeep, with a peripheral speed so great, that the material treated is with difficulty guided under the runners, and is swept to the rim flange and over, instead of through, the perforated grids by the excessive centrifugal action thus set up. It is possible to keep within the limits of edge runners, while producing a satisfactory material with economical results, by having the machine correct in design, properly constructed for size and grinding weight, driven at effective speed, fed with reasonably dry material previous-

ly sized through a jaw breaker, and supplied in amount suitable to the capacity of the mill in a regular flow from a receiving and storage hopper, by means of a plate belt; or in case of two or more bodies being used, a Rasquin and Jooris type combined body-mixing and mill-feeder machine, consisting of a plate belt in correct ratio for the required body, and timed to give the required quantity to the pan. Greater output with less wear and tear for less consumption of power, and a better product are assured.

The Multiple Runner Mill for difficult plastic clays has found favour on the continent, and is built by at least one English firm.

The pan which revolves is made with three runner paths adjacent to each other and formed at different levels, the highest being towards the centre of the mill. The distance between the roller and path gradually decreases, the last roll running in contact with the path. The feed is delivered on to the inner or highest path, and after being ground by the smaller roll is passed, by means of scraper ploughs, on to the middle and lower paths, being similarly treated at each stage respectively and finally discharged from the machine. It is claimed that the treatment is equal to that of three mills. This cannot be, however, as the breaking up is nore effective in the separate mills. Nevertheless, there are many clays for which this type of mill would give most helpful treatment, as it takes less foundation space than a series of single mills. The makers further claim economy of motive power and reduction of wear and tear. The figures quoted are 15 B.H.P. for an output of 5,000. The approximate weight of the mill being 13 ton 16 cwt. Both sets of figures correspond to about one-half of those common in English practice.

Edge Runner Mills for Wet Grinding.

The Edge Runner Mills is used for wet grinding for medium fine products of a granular nature. Well known examples are the slow speed and high speed Chilian Mills, the former having two and the latter three runners, while the pans range from 5 to 6 feet in diameter. These mills find their sphere of usefulness in reducing ores. Their long life and comparative freedom from reapairs allow them to run continuously for long periods. Wet grinding pans are used, similar in construction to edge runner dry grinding mills, but with less area of perforated bottom, for dealing with tough, wet, and sticky clays, the product being forced through the openings by the action of the scrapers. Such clays are sheared and disintegrated by the action of the runners; in some cases the grids alternate with the segments of the path of the runners, the clay being pressed through as it becomes sufficiently reduced. The product is then finally ground by roll mills.

In American practice it is usual to find dry-pan and wet-pan mills side by side, the one forming the reducing unit, and the other the mixer (see Fig. 11). The dry pan delivers into overhead

breaker hoppers from which the wet pan obtains its supply. The wet mill is not essentially a grinding or reducing mill, although such action to some extent does take place; but it is a mixer, and, as such, it is out of the range of this paper.

In Fig. 11 the runners have the wearing rims double-coned inside, and locking with a collar and bolts, thus dispensing with the usual wedging. The grids are built up of a series of concentric arcs spaced to give the openings, the distance pieces limiting the length of the slots. Such a method would give long life, but the efficiency would be reduced, and the product anything but uniform.

Grinding by Rolls.

(Figs. 12 and 13).

Grinding rolls effect reduction by the shearing action of two discs, the diameters of which are determined by the size of the fed material, and the length by the output required. They revolve with their shaft axis in the same plane, and the direction of their periphery inclined toward each other. The rolls work parallel, and are spaced apart according to the ratio the grinding is required to give; this spacing is called the set of the rolls. The space above the centre line of the rolls within the angle of nip is the throat, and that below is the discharge of the machine. The grinding is carried out on the rolls by the toggle action. Material fed into the throat is seized by friction, and passing down to the set, is broken by the pressure and shearing exercised by the surfaces of the rolls. The all important factor (other things being equal) is the ability of the roll surfaces to take hold of the material. The diameter of roll, and the material finish of the roll surface are the telling factors that go to make greater output, and give quality to the sizing of the product. In roll mills, sliding of material unnecessarily wears the face of the roll and hinders output. Sizing of the maximum pieces of the feed is, therefore, important, and this factor must be determined beforehand. The work done is brought about by seizing of the material by the rolls. This will be done when the wedge angle obtained is equal to, or less than, the nip angle. This angle is the sum of the two sliding angles of the material, the outer arms forming tangents at the points of contact where the largest pieces to be ground touch the roll surface. In many instances, this factor may be helped by the surface of the one roll being roughed (according to the coarseness of the product), and (or) the spread of the two rolls being different. It should be understood that the angle of nip depends on geometrical factors to be fulfilled by the governing size of the material to be ground, the diameter of the rolls, and the spacing or set of the rolls. For the same diameter and the same "set," it varies directly with the size; pieces above a certain size will not be seized unless one of the other factors is modified, For the

same diameter and same size of fed material to be broken, it varies inversely as the set. For the same set and same size of fed material it varies inversely as the roll diameter. The speed factor will modify these conclusions. Much thought and application have been given to grinding by rolls in recent years, resulting in advance in economy and output in relation to power absorbed, quality of grinding, and quantity of output. There are many good machines on the market suitable for a wide range of materials; hence, by using discrimination, adequate results are assured.

Roll grinding is advantageous if these limitations are observed when the plant lay-out is designed. They are best used as secondary units receiving the product from jaw breakers or gyratory breakers; and although they are capable of breaking pieces, the size of 6 inch cube, it is false economy for them to deal with pieces larger than 2½ inch cube, with a reduction ratio of 4:1. The length of the grinding rolls should not exceed one half of their diameter, any length above this proportion causing excessive stresses and wear on the shaft and bearings. The life and the output efficiency of rolls are increased by care in regulating and distributing the feed, so that the whole length of the roll is fully employed. Consistant sizing will only be possible if the "set" is evenly maintained. Driving pulleys having heavy rims are helpful in absorbing shock, and in distributing the wear and tear of bearing parts. Especially should they be used when the sizing of the feed is not necessarily uniform.

Geared Rolls, generally spoken of as Cornish Rolls, consist of a double roll-crusher having the driven roll carried by fixed bearings, and carrying a spur gear wheel to drive through a similar spur wheel, the opposing roll running in bearings with sliding bases, which are adjustable by packing pieces to give the required amount of set. This distance is maintained by compression springs acting directly in compression on the sliding pedestal in the older design, or acting through tension rods to a crosshead spanning the width of the machine, in the modern type (see Fig. 12). This type is the better disposition, as the frame of the grinder, being mostly built in cast iron, is put into compression. The provision of further opening of the rolls is necessary on account of tramp iron. Geared rolls can only be run at moderate speeds of 15 to 25 R.P.M.; they produce from 4 to 8 tons per hour when reducing 1½ inch up to 2 inch cubes to ½ inch and smaller, and require from 10 to 20 H.P.

Standard Belt-Driven Rolls. The mechanical efficiency of this type is higher than that of the geared rolls, since it gives a larger output for the same H.P. Both rolls are driven, and the belt wheel rims, being heavy, compensate the shocks produced by the seizing of the feed, give more uniform running, and allowing higher speeds to be run with safety and economy. Periphery

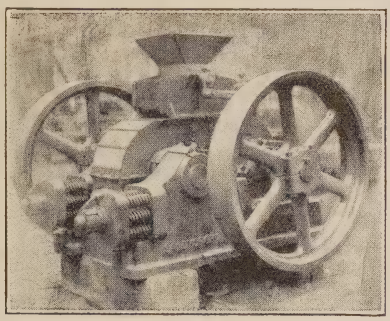

Fig. 12.

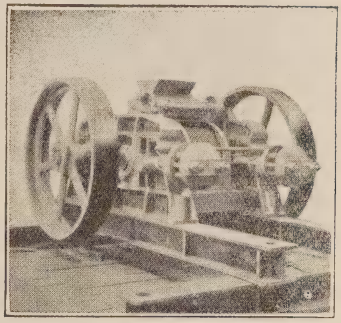

Fig. 13.

speeds vary between 500 and 600 feet per minute, thus giving an output of from 10 to 16 tons per hour with a reduction of 4:1. The housing of the rolls is similar to that of the geared type. Provision for long belt drives should always be made, thereby giving longer life, greater elasticity, as well as tending to lessen shock at the bearings. There should be a difference of diameter in the belt pulleys on the rolls of at least 10 per cent. This makes the angle of nip more effective, tending to turn over the oversize feed until a more favourable face presents itself to the throat of the mill, and making for less wear of the roll faces. High speed rolls are used for fine reduction with a large output. As the set of the rolls is restricted, higher periphery speed must be attained if the capacity is to be maintained; the usual periphery speeds are 1,000 feet or more per minute. The width of face is reduced, and rarely exceeds 6 to 8 inches; for efficient work the face must be kept free from grooving, and must be set parallel. The machine will then produce from 6 to 10 tons per hour, at a reduction of 6:1, for an expenditure of 20 to 30 H.P. In these mills a difference of speed as high as 2:1 is used, the fixed roll carrying the larger pulley; the pulleys on the line shaft are of equal diameter. These mills are encased with a movable housing, which has a feed hopper at top, and forms a discharge chute at the bottom. It is necessary to have large diameter shafts and bearings of ample length. The framework should be sturdy, and the sliding pedestals coupled to the resistance springs by heavy, forged tension rods.

Rolls for grinding mills should in all cases be provided with removable rims, called shells or tyres, of special steel, carried on a core of cast iron. These two parts are secured to the shaft in various ways; the most reliable type have double coned contact surfaces locked with a coned loose bush bolted through the core of the roll. Relatively thin tyres have been shrunk on to parallel cores and trued up, and have given very good results. When worn there is no difficulty in bursting them off and replacing them.

Grinding by roll mills should receive much greater application than has yet been the case in the preparation of refractories. The edge runner mill has monopolised this branch beyond its economic limits; it is the only reduction mill for all purposes found on firebrick plants, with, perhaps, a solitary exception. Roll mills may possibly come into use now that grading of material for bricks to stand higher temperatures and compression is becoming a necessity. The product of roll grinding is granular, and the modification of sizing is under easy control. In all cases the wearing shells of rolls for high duty should be of manganese steel. This class of steel gives a longer life, and the uniform wear maintains a product of regular quality, two necessary requirements where large and continuous output is needed. These mills require little supervision; they need only a definite feed, periodical inspection and sufficient lubrication. The foundations should be well proportioned, and the mill easily accessible.

XXVII.—Machine for Coating Tiles with Enamel Glazes.

By Clifton Reynolds.

THE purpose of the machine, which is the subject of this paper, is to coat tiles with glazes. This process is, as far as I am aware, usually carried out by hand.

The principle I have adopted in this machine appears to be novel to everyone to whom I have so far demonstrated or explained it. This is very surprising to me because the method is really very simple. Probably some of you, like myself, have seen a similar method, although in a much cruder form, used abroad. If so, they will probably agree with me that tiles produced under those foreign conditions would not be suitable for the trade of this country. I have endeavoured—and it will be for you to judge with what success—to improve this principle in order to produce the high standards of quality demanded in this country. I should imagine that it is not unusual for newcomers into this industry to rush in "where angels fear to tread" with ideas for improving methods which, on the surface, appear to be antiquated and inefficient. Perhaps a few survive. Your criticism, which I hope you will express, should therefore be valuable to me.

My own observations of the difficulties encountered in connection with the manufacture of Enamel Tiles may not have been made under conditions which are common to all tile works, but they have led me to regard this operation as rather too costly as to labour charges and a little too hazardous in regard to the uniformity of production which is so imperative in the manufacture of tiles.

Apart from differences of practice on different works, there are doubtless differences of customers' demands consequent upon the varying nature of the trade which any particular tile manufacturing firm may concentrate upon, and, of course, other circumstances which lie outside the scope of my paper. But whatever standards of selection have to be encountered, some at any rate of the troubles I have seen must also be experienced by all manufacturers. Prominent amongst these difficulties have been, first, that of providing skilled labour in this department; second, of making it proficient and profitable; third, of retaining it when it is so developed.

In the course of investigating many failures in hand dipping, I was led to the conclusion that these, like many others in potting processes, were accentuated by the number of factors which are, more or less, left to the skill of the operative. In a business where the slightest variation from a sample shade means that

goods produced are almost valueless, it appears to me that it would be useful to make certain as many of these factors as possible. In hand dipping, granted a glaze of known weight per pint is issued to the dipper, the glaze in his basin is settling all the time, and when I have taken the first tile after a stir and compared the weight of glaze on it with that on the last, before the next stir, there is often a serious difference. The duration of the moment of immersion, also left to the skill of the dipper, has likewise to be considered. Skill is also required in taking the dipped tile away from the surface of the glaze by hand to avoid thick lines made by the parting of the glaze on the tile from the glaze in the basin. This I have found to be a particular difficulty with eggshell glazes.

To eliminate these uncertain factors, any machine must, therefore, be capable not only of controlling to a fine degree the weight of glaze delivered, but must also be capable of accurate adjustment as to the time occupied in delivering it. With such a machine it should be possible, merely by readjusting it to a given setting, to repeat with certainty any result desired, provided, of course, that firing conditions do not vary.

Such a state of affairs can be achieved approximately enough for practical purposes, as all those in the tile trade know, with what I will call the American Dipping Machine, but the use of this, for the purpose under consideration, is prohibited, for the majority of orders at any rate, by one objection, namely, the amount of time and labour required to clean up in order to change from one glaze to another. An enamel dipping machine must, therefore, be capable of quick changes.

The machine (see fig. 1) consists of a conveyor made up of rollers set at such a distance from each other that they will, when rotated in the same direction, carry forward from one to another, a board, along the upper surface of which tiles are placed. The tiles are held in close contact with each other by means of a spring and no glaze can fall between them (if they are reasonably square).

There is provided a glaze feeding device capable of producing a perfectly even fan-like stream, the strength of which can be finely controlled. The bisque takes up all the glaze ever required, for the stream falling evenly across the entire width of the tile will cover the tile in any required time by accelerating or retarding the speed at which the tile passes through it.

Surplus glaze will fall over the outside edges of the tiles overlapping the boards and will be received in a suitable vessel underneath for return to that above. If it is desired to remove glaze from the edges of the tiles this is very simply done by knife edges impinging by adjustable springs on the edges of the tiles as they are propelled by the conveyor.

The filling of the boards, which so far I have only done by hand against a simple gauge, could, of course, be done quite easily

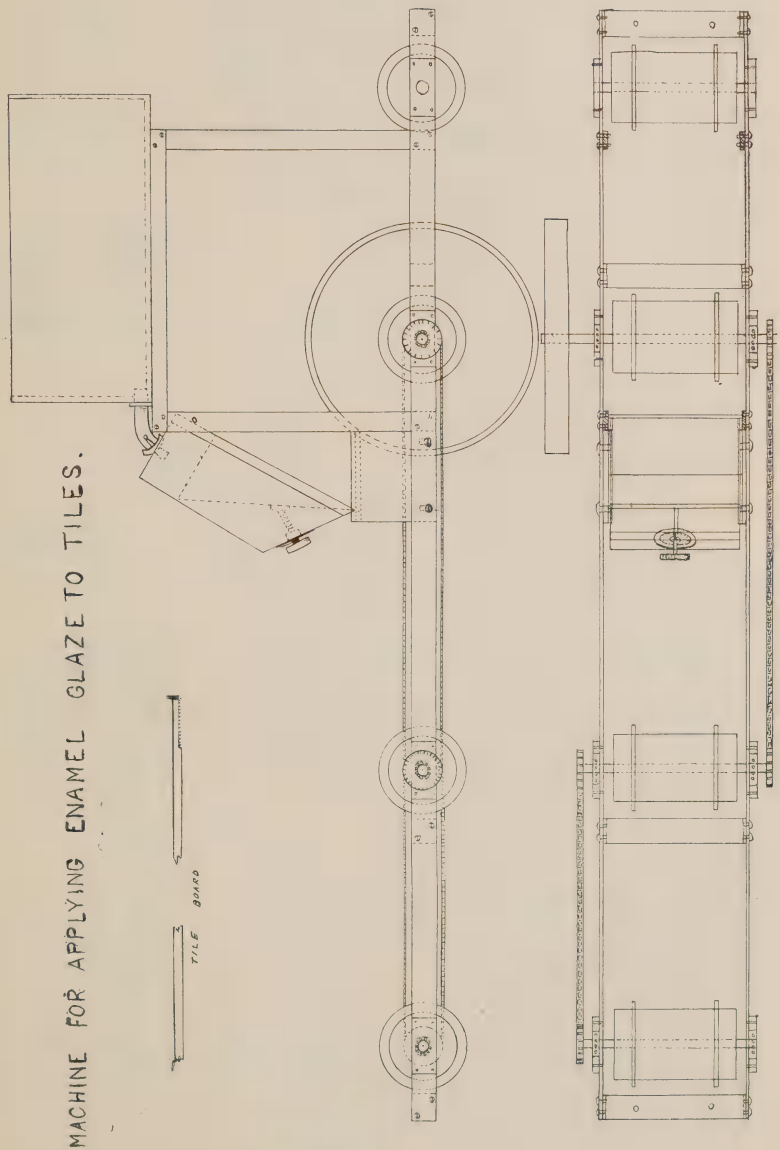

Fig. 1

by mechanical means. I think it is necessary to remove the dipped tiles by hand.

From actual experience in dipping a good many hundreds of yards of various sizes of tiles, I estimate that three girls, whose total wage is less than that of one skilled dipper, can produce at about one seventh the cost of hand dipping. Twelve boards, carrying one quarter of a yard each, making a total of 3 yards, can be treated in about five minutes. The quantity of glaze falling whilst three yards is passing through the machine is convenient for recharging. With sufficient labour to keep the machine constantly supplied with full boards the speed of output would be enormous. There are no working parts whatever to clean in this machine when it is desired to change to a different colour. The glaze-delivering hopper can be swilled under a tap in a few seconds, it readjusts itself automatically. Mechanical agitation of the glaze can be added without difficulty, but it is questionable whether this is necessary.

The advantages claimed are summarised thus:—

1. Accurate adjustment of the thickness of glaze on the tiles, (this helps matching).
2. Even surface of glaze all over each tile, (this gives uniformity).
3. No skilled labour required.
4. Speed.
5. Economy.

This machine will not, however, pick out a tile which happens to be hard fired and put the same glaze on it.

The illustration given here is that of a small model constructed not for production purposes, but in order to demonstrate the principle only. There are many obvious additions capable of introduction to a machine designed for actual production.

XXVIII.—Notes on Fritting.

By S. R. Hind, B.Sc., A.R.C.Sc., A.I.C.

It would be no exaggeration to say that, in every process of pottery manufacture, the energy theoretically necessary to achieve the desired end is scarcely a tithe of that actually expended in production. Undoubtedly, this is due to the extraordinary difficulty of working with complex, and little understood, materials, and of producing articles of such delicacy as those resulting from the potter's art. Nevertheless, these difficulties should always constitute a challenge to us to seek improvement in every possible way. What past generations of potters have accomplished must not be taken as final in any sphere of the industry. Indeed, the present generation of potters will not be worthy of the past, if they do not show even more energy than their great predecessors in combating the difficulties confronting them.

This paper deals only with one small, but important aspect of the industry—namely, fritting, and the author wishes to bring to your notice a new development which is rapidly gaining favour in the United States, and which has already obtained a footing in this country.

First of all, it would be as well to go into some of the principles involved in fritting.

Thermal Efficiency of Fritting.

With regard to fuel-consumption, we need a basis or reference. How much heat is really needed to do the work of fritting? The scientific data required to estimate this are, unfortunately, very incomplete, and the heat required, in any case, varies greatly according to the mixture being fritted. Nevertheless, such estimates as are possible show how minute a proportion this heat bears to the total generated in any frit kiln. Using coal of a calorific value of 11,700 B.Th.Units, it is estimated that—

a borax frit required ..	8·0	per cent. of its weight of fuel.
and a lead frit required	3·3	,, ,, ,, ,, ,,

The frit-kiln actually uses about 30 times as much as the first of these figures. Even then, in the above percentages, no allowance has been made for a possible utilisation of the heat in the molten frit leaving the kiln. It can be taken, for present purposes, that the cost of this heat is so small as not to warrant attempts at its recovery.

Effect of Fuel on Design.

The design of all kilns depends to a large extent on the nature of the fuel consumed, particularly where, as is usual, the goods undergoing treatment must be contaminated as little as possible by the fuel or its bye-products.

Where coal is the fuel, as in ordinary frit-kilns, a grate is

required to retain the ashes. Its area is regulated by the rate of combustion required and its depth depends on the nature of the coal and on the type of flame in the furnace. Also, the designer of the grate has always to bear in mind that the total capacity of the firemouth shall be large enough to carry on between baitings of reasonable duration, and also, in certain cases, to allow of the accumulation of a suitable amount of clinker to restrict the air-supply at the stages of firing when the draught has considerably increased. Coal-fired frit-kilns are operated by the draught of a chimney—a feature which tends to increase the wastage of heat, and one which may be dispensed with, where other types of fuel are used.

Where coal has been used to make producer-gas for fritting, the generators still bear a considerable resemblance to the ordinary fireboxes. In fact, with the semi-producers which are used for this purpose, the difference is largely one of degree. All the firemouths normally used for kilns and ovens act to a notable extent as gas-producers when the fuel-bed is deep and the air supply suitable. This is usually the case during the later stages of firing. Semi-producers are, on the other hand, most readily started up as open fires, which are afterwards banked up to give the gas-producer conditions. Pulverised fuel is at present not promising, on account of the special means required for ensuring separation of ash dust.

Now, if we consider the conditions for burning liquid fuel (such as petroleum fuel oils) and gaseous fuels (natural gas and town's gas), we shall see that at least two important differences occur:

(1) The fuel is most conveniently supplied under positive pressure, thus readily giving a very high rate of combustion, and also eliminating the need for chimney draught. Perfect control is possible, both as regards fuel and air supplies. This is a tremendous advantage.

(2) No provision is required for ashes or clinker, as earthy impurities are practically non-existant. The fuel can then be fed through a jet into the furnace and burned in as close proximity to the goods to be heated as is consistent with obtaining the correct type of heating.

Moreover, the positive-pressure jet method of feeding fuel into a furnace gives a further great advantage in making it possible to isolate the burner, in a mechanical sense, from the furnace. The latter is then free to rotate and move in various directions without affecting the adjustment of the pipe-line, etc., of the fuel-jet.

We thus have three types of fuels, which will all do the work of fritting, viz.: solid—coal; liquid—various fuel oils derived from petroleum, and gaseous—natural gas, town's gas, cleaned producer-gas.

Of these three states, the liquid and gaseous are distinctly the most attractive from the points of view of design and of possible thermal efficiency. The choice of fuel, and the design dependent upon it, of course, ultimately rest on the cost—that is, cost of fuel, cost of labour and cost of equipment.

During his recent visit to America, Dr. Mellor had brought to his notice a frit and enamel kiln specially designed for use with oil or gas-fuel—the U.S. Rotary Enamel Smelter. The author is indebted to Dr. Mellor for information concerning this kiln and for valuable suggestions.

An attempt has been made to compare the cost of running this, the U.S. Rotary kiln, with the ordinary coal-fired frit-kilns of this district. For this purpose, Mr. A. Heath has kindly supplied fritting costs on the latter, coal-fired kilns.

Relative Costs of Fritting.

The costs are greatly influenced by the time taken in fritting. The makers of the U.S. Kiln state quite definitely that a charge of 750 lb. of raw batch can be fritted in the No. 4 kiln, as a general thing, in 45 minutes, and that the kiln is then ready to use again without delay. The period is increased to 60 minutes when starting from the cold state. Without further information, the author does not, however, feel justified in predicting that the fritting time could be reduced so greatly as this would suggest, without injury to the product.

On the other hand, there is no doubt that the method of operation of the U.S. Kiln is calculated greatly to reduce the time of fritting, and there can be little doubt that, up to a point, this is beneficial in preventing volatilisation of certain constituents of the frit. For this reason costs, etc., have also been computed for a fritting-time of three hours. The following estimates are, of course, subject to variation according to the frit in question.

The cost of the No 4 U.S. Rotary furnace, as recommended for use in potteries, together with the necessary blower, motor for rotating the furnace and oil-pump, amounts approximately to £560 on the rail at the American works. On the same terms, a new lining costs about £24, plus cost of brick-laying. No doubt the equipment could be assembled at less cost by buying all accessories in this country. The lining should last for as big a turn-over of frit—even longer appears to be common—as in the ordinary kilns. The wear is quite even, as the rotation of the furnace ensures that the difference in temperature between the refractory lining and the frit is small and also the lining is probably protected by the film of glaze which completely covers its surface. The rate of fritting being so rapid in the rotary furnace tends to reduce the wear on the lining per charge of frit.

	Coal-fired frit-kiln	U.S. Rotary Kiln	
		45 min. period (normal)	3 hr. period (special)
Fuel.			
Cost per ton of finished frit ..	92s. 5d.	20s. 10d.	65s. 2d.
Percentage saving over coal-fired kiln	—	77%	29%
Labour.			
One man only is needed to carry out the whole of the work on a No. 4 kiln-charging, fritting and running off. Where several furnaces are employed, the same man is able to control them all.			
Cost per ton of finished frit ..	24s. 2d.	5s. 8d.	13s. 3d.
Percentage saving over coal-fired kiln	—	77%	45%
Normal output of frit daily ..	—	4,900 lb.	2,100 lb.

Quality of Product.

There never appears to have been any doubt about the high quality of the product obtainable from the rotary furnace. Samples of white and of black enamel examined were very satisfactory. These were smelted by the "Defiant" Enamel Tile Co., of London, and here the period of smelting in some cases reached three hours. This firm appears to be quite satisfied with the rotary kiln. Oil fuel is used in this case and is found to be cheaper than town's gas. You will be better able to form an opinion of the superiority, or otherwise, of a rotary kiln in point of quality from the general description of the Rotary kiln and its method or operation.

The U.S. Rotary Kiln.

Fig. 1 shows a view of the kiln during pouring operations. The furnace consists of a cylinder of steel tapered at one end to the charging hole and fuel-injector and at the other to a circular aperture which serves during the run as an outlet for products of combustion, etc., and later as a pouring-hole. The case is lined with suitable refractories and forms, as will be understood, a rotary open-hearth furnace. It is firmly supported on castings bolted to a firm foundation, and is balanced on a pivot allowing the whole furnace to be tilted by hand for pouring off the frit. Below the furnace is the usual tank of water, into which the enamel or frit is poured. The middle of the casing is girt with a crown-wheel geared to a pinion, so that the furnace can be rotated slowly on its own major axis. The supply of fuel-oil (or gas) and air are controlled to a nicety by appropriate hand-wheels on the burner. As much head-room as possible should be allowed for

the furnace on account of the necessarily high temperature of the products of combustion. Where space is limited, or offensive fumes are given off from the frit, it is advisable to provide a sheet-steel stack over the pouring end of the furnace. The furnace is made in a number of sizes, from a laboratory type dealing with a 60 lb. charge up to the largest, dealing with 1,100 lb. at a time. A No. 4 furnace dealing with a charge of 750 lb. is found suitable for use in potteries.

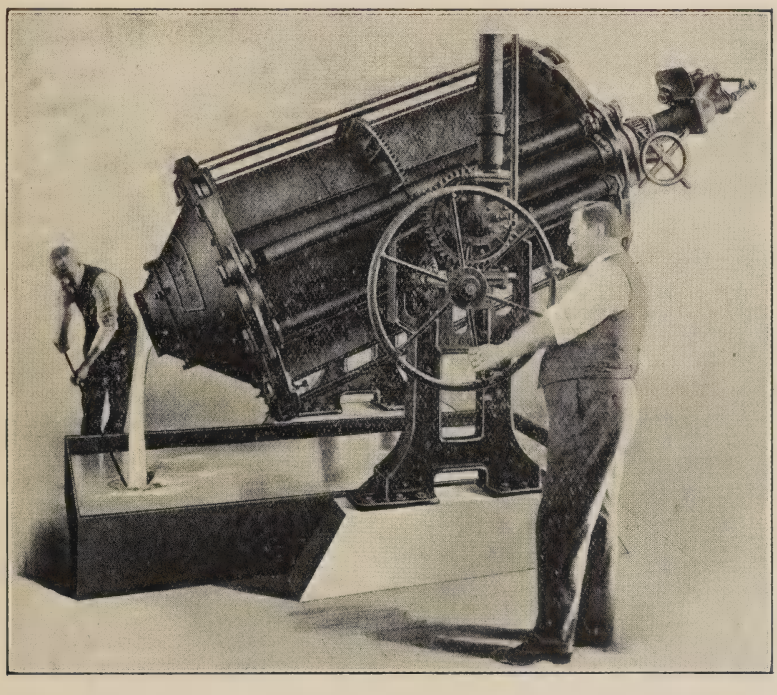

Fig. 1.

The operation is quite simple. The charge, preferably ground in a ball-mill, is shovelled into the furnace through a charging-door in the burner end of the furnace, the latter being in its normal, horizontal position. The burner is then started and the furnace rotated slightly on its axis, until the charge lies at its greatest angle of repose. The heat melting the batch on the surface causes the molten enamel or frit to run down the inclined surface and collect in a pool in the bottom of the hearth. As the batch melts, the furnace is so rotated as to bring up a continually

fresh surface for melting. The whole batch having melted, the furnace is then slowly and continuously rotated in the same sense, by hand, or preferably, with commercial furnaces, by a small motor, until the charge is matured. The heat-treatment of the molten mass must be extraordinarily effective, as the melt is in continual motion, and the heated lining of the furnace is descending regularly into the melt and giving up its heat. This also means that the lining is never overheated to the extent that would occur with a stationary furnace, and, combined with the protective effect of a coating of glaze on the lining, results in conditions which tend greatly to lengthen the working life of the lining. Samples of the melt can be withdrawn by way of the charging-hole without stopping the operation. The batch having matured, the furnace is tilted up and the charge run off into the water-tank below. This is accomplished under perfect hand-control and the loss by frit left in the kiln is neglibible, as the kiln is finally drained in a vertical position. The furnace is then levelled and is ready for immediate re-charging.

It should be pointed out at this stage that, in the melting of a frit, there is always a liability of loss through dust or finely-ground batch-material being blown out of the kiln. This risk is rather more serious in the case of a blast-operated kiln, such as the Rotary Kiln.

The bearing of the method of operation of the kiln upon the quality of the product is well brought out in a reply by the makers of the rotary furnace to the question: "Why do you claim it turns out superior enamel? ". This is substantially as follows and the remarks are largely applicable to any frit:—

"According to reports received from.....users, this equipment produces an enamel which is far superior to that produced from the old brick smelter. It is far more homogeneous and uniform, has a higher and better gloss, has greater opacity obtained through a minimum amount of opacifying agents, is free from all contaminable material, reduces rejections to a minimum, reduces fish scaling and chipping, providing, of course, the formula is well balanced and the coefficient of expansion correct, it can be applied to the ware with a lighter coat and yet obtain the same results and appearances of a heavier coat, and burns more evenly and uniformly on the ware."

"To prove the above assertions, it becomes necessary to compare the method of smelting in the U.S. Rotary Furnace with that of the old brick smelter. The production of a more uniform and homogeneous product is of prime importance and can readily be accounted for by a comparison of the methods of smelting."

"When smelting enamel in the ordinary coal-fired kiln, it becomes necessary to melt the raw batch by force of heat through a non-conducting charge from above downwards, that is, an excessive

degree of heat over the fusing temperature of the batch is needed on the upper portion or crown of the smelter to fuse the top portion or layer of enamel gradually. This fused layer gradually conducts the heat, to a limited degree, to the layer below, and so on, until the bottom of the charge.....is reached. This process in itself seems practicable at first thought, but when going further into the matter we find the following very detrimental conditions:"

"The heat applied by the flame and the heated portion of the brick lining applies itself to the enamel batch in a curved form, which enables the centre of the charge to become subject to an excessive heat, leaving the sides in a somewhat unfused condition. This excessive heat applied to the centre of the batch naturally causes local surface overheating, but still leaves the sides or outer portions in a more or less raw or unfused condition. To fuse the outer edges of the batch thoroughly, particularly that portion which lodges in the four corners, requires a greater heat, a longer time, and consequently, a greater fuel consumption. This naturally has a detrimental effect on the fused centre section of the batch, which is now already matured, and causes this to be overheated, while the outer sections are yet in an unmatured condition."

"To overcome this unsatisfactory procedure, hand-stirring or rabbling is employed, but this is also objectionable and the result is, that the entire batch is not uniformly fritted. If this hand-stirring were done at regular intervals the condition of the batch would not be so bad, but this stirring now mixes the fused with the unfused and it is, therefore, impossible to produce a thoroughly uniform and homogeneous product. Moreover, it is impossible, when stirring, to reach into the corners of the kiln; hence a portion of the batch is left in the kiln. This accumulates, heat after heat, until a considerable loss is suffered in this manner."

"The failure to drive off *all* the volatile gases in the raw batch ultimately shows up on the finished ware in the form of raw spaces, poor gloss, etc. Moreover, the constant excessive heat applied to the crown of the coal-fired kiln, together with the fumes of the enamel, gradually causes the disintegration of the crown, on which some of the products of combustion, caused by improper firing, particularly when using coal or coke as fuel, are deposited. This is liable to fall into the enamel batch, causing black specks in the finished ware."

"For the correct fritting of enamel, especially when metallic oxides are used as opacifying agents, a thoroughly oxidising fire is needed, and this is extremely difficult to obtain, maintain and control in the coal-fired kiln. The result is that, at various periods during the fritting process, especially when refiring, a reducing atmosphere is produced, which turns such chemicals as tin oxide, etc., into the metallic state. This in turn shows up as ruby spots and other discolorations in the resultant ware. It is

at this period, when the batch is subject to the reducing atmosphere, that particles of carbon or the like, caused by improper and uncontrolable firing, are deposited on the disintegrated crown and later fall into the enamel batch causing black spots. This is true when using oil or gas as fuel in the ordinary frit-kiln, and more so with coal and coke."

"In order to show how the U.S. Rotary Kiln overcomes these objectionable features, it will be necessary to explain the method used by it in smelting enamels."

"After the charge has been made into a preheated furnace, the smelting chamber of the furnace is partially rotated so that the batch lies at an angle of approximately 35°, or to its reposed position. As soon as the burner is relighted, the enamel commences to melt or fuse and flows down this inclined furnace to the bottom of the furnace forming a bath and leaving a fresh surface of the raw batch exposed to the heat. This process embodies two advantages:—"

"1. The melted enamel is free from any danger of overheating, for it is being constantly kept close to the fusing point of the charge. The melting chamber of the furnace is also held at the same temperature, due to the fact that the burner is so constructed as to maintain the desired temperature, and only sufficient fuel is used to obtain the fusing temperature of the charge. Any excessive heat is absorbed by the raw batch remaining unmelted in the furnace."

"2. The unmelted material is always exposed directly to the heat, reducing the melting time and consequently the fuel consumption."

"The partial rotation is continued, that is, as the slope of the unmelted material becomes less and the melted enamel does not flow freely to the batch below, the melting chamber of the furnace is again partially rotated to increase the angle and to bring the raw material back to its reposed position. This partial rotation is continued from time to time until the entire charge is fused. After this is accomplished, the rotation of the melting chamber is continuous, causing the white-hot lining from above to be brought below the bath, thereby delivering heat from below, supplementing the heat applied from above. This continuous rotation, whereby a double heating process is employed, that is from above and below, causes the melted bath to obtain a uniform temperature throughout, which in turn, causes a circulation of the melted bath and the liberation of all volatile gases. This procedure quickly increases the temperature of the melted enamel, expels the volatile elements, and produces an uniform and homogeneous product."

"As we have stated, the correct method of melting enamel in order to secure a perfect product, requires a thoroughly oxidising fire. This is easily obtained, maintained and controlled by the construction of the entire furnace and burner. We have pre-

viously explained the method used in the atomisation of the fuel and air in order to produce perfect oxidizing conditions, and to avoid the presence of any products of incomplete combustion. You can readily realize that the deposition of carbonaceous material on the crown of the furnace cannot take place when complete and perfect combustion takes place."

POSSIBLE FURTHER ECONOMY.

In view of the high temperature of the products of combustion from the rotary furnace, it is obvious that a considerable amount of heat should be recoverable from this source. A rough estimate showed that the heat in the products of combustion would be equivalent to quite 35 per cent. of the oil burned. Now, in a works using several of these furnaces, recovery of this heat in the form of steam would be quite a practical proposition. A waste-heat boiler, which might be coupled with some equalising device, such as the Ruths Steam Accumulator, would afford a steady supply of steam at moderate pressure. The quantity of steam generated, must, of course, be estimated to suit the case, but the following figures should be of some assistance:

Let us allow for a 60 per cent. efficiency of the waste-heat boiler, working on *one* No. 4 furnace. The normal 45-minute to 60-minute period of fritting will give 4,100 lb. of steam from and at 212°F. daily. With the longer 2½-to 3-hour special runs, the steam produced will increase to 5,900 lb. daily. All working should lie between these limits and nearer the former.

DISCUSSION.

MR. A. HEATH:—I think this kiln is only used for soft iron enamels. Is that so?

MR. HIND:—No, it is also used for pottery glazes.

MR. C. D. GRIMWADE:—Will Mr. Hind indicate what pressure is applied to the oil or gas supply? It seems that the difficulty will be in avoiding the frit being blown out of the kiln. The loss of frit by draught is bad enough in the ordinary kiln, but in this type, where there is a confined space, it looks as if the loss will be serious.

MR. HIND:—The loss of frit in the way Mr. Grimwade mentions is certainly likely to be a weak point in certain cases, but one that might be remedied without much trouble. It is worth while noting that the rotary kiln is designed to cover the powdered charge very rapidly with a film of sintered to liquid glaze and this, subsequently, completely protects the charge against loss in the manner referred to.

MR. CODLING:—What is the price of fuel oil in this country, and what are the sources of supplies?

MR. HIND:—I am informed that in June, 1924, the price of Shell Mex fuel-oil delivered in 10-ton lots at Manchester was

97/6 per ton. What the price is to-day I cannot say, but you will have no difficulty in finding this out.

MR. MEREDITH:—What space would be required to house the kiln?

MR. HIND:—The No. 4 kiln requires a floor-space of 12 ft. × 11 ft., the No. 4B, a space of 12 ft. × 13 ft.

MR. F. TURNER:—I should imagine that the figures given would not apply to the ordinary frit kiln to-day. They appear to be rather high.

The point raised by Mr. Grimwade is very important and the loss by draught is considerable in a frit kiln. If you reduce the draught the loss will also be reduced.

If the Rotary Kiln is what they claim it to be, it is a most important thing. The modern frit kiln is not ideal by any means, and I should like to suggest that fuller information be obtained as to the high pressure applied in the Rotary Kiln. I presume that might be obviated by using gas instead of oil. I should also like to know something of the relative costs for firing with frits as we understand them. One cannot judge things satisfactorily from these figures, for there are mechanical arrangements which need adjustment and there is the question of the renewal of the lining and so on. Furthermore, what happens to the casing when the lining begins to go? What is the temperature of the room where you are fritting?

Would it be possible to have information about any kilns of this type installed in this country?

MR. HIND:—I am very glad that such a keen interest has been aroused by the remarks I have made. I should like to refer Mr. Turner to the Power Engineering Co., of Trafford Park, Manchester, for further details of the Rotary Kiln, and also for the addresses of firms using the kiln in this country.

MR. RICHARDSON:—I should like more particulars regarding the costs. I take it that these costs are for 1920. There would be no difficulty in getting this data up-to-date, and I suggest that this be included in the TRANSACTIONS.

MR. HIND:—The fuel-oil price I have given. The coal used in the ordinary frit kiln on which Mr. Heath based his costs was reckoned at a little less than £2 per ton (11 3 ton 19 cwt. £220 5s. 7d.). I have made many inquiries in the Potteries for further data on ordinary costs of fritting; the result has been disappointing.

XXIX.—Note on Whieldon Pottery.

By W. Emery.

POTTERY collectors are not as a rule concerned with the beauty or technical value of their specimens. It is sufficient for them to know that there exists only a limited number which cannot possibly increase, but may very well decrease. In the case of Whieldon ware, however, the majority of specimens possess artistic beauty and also reach a high technical standard.

Thomas Whieldon was born in September, 1719. There is no record of his early career, but it is stated, on very reliable authority, that he was in business as a potter in Fenton Low in the year 1740; that is to say, he was a manufacturer on his own account by the time he had reached his majority. Fortunately for the student of Whieldon Pottery, one of his note books is on exhibition in the Hanley Museum. Many abstracts have been published from time to time by various writers, especially as regards his connection with Josiah Spode, the founder of "Copelands," Astbury, and other noted potters.

The following interesting items from his note book may be contrasted with charges for similar services under modern conditions:—

		s.	d.
1749.			
Jany. 27.	Hired Jno Austin for placing white, etc., per week	5	6
Feb. 20.	Hired Wm. Cope for handleing and vineing and cast ware for	7	0
June 2.	Hired a boy of Ann Blowrs for Treading ye lathe	2	0
1751.			
Jan. 11.	Hired Elijah Simpson for Turning, he is to have per week	8	0
Jan. 11.	Hired Saul Jackson for Throwing Sagers and fireing, per week	8	0
Oct. 26.	Hired Cupit	2	3
	Pd earnest	0	6
	I am to give him a old pr of stockings or something.		
1753.			
Aug. 29.	Hired John Everal, per week	4	0
	Pd earnest 2 pr Stockings	4	0
	1 shilling in cash..	1	0
	To have a handkerchief.		
1749.			
April 9.	Hired Siah Spoade, to give him from this time to Martelmas next, 2s. 3d. or 2s. 6d. if he deserves it.		
	2nd year	2	9
	3rd year	3	3
	Pd full earnest	1	0

The great Josiah Wedgwood was a junior partner with Whieldon for the five years 1754-1759. Some uncertainty has arisen as to the date of the latter's death. In Jewitt's "Ceramic Art of Great Britain," the year is stated to be 1798, whereas P. W. Adam has shown that Whieldon died in March, 1795, and that his will was proved May 18th, of the same year. The Fenton Low works were closed in 1780.

Having for a number of years been interested both in the literature and the products of the earlier potters, I was delighted to find, in November, 1924, during one of my periodical visits to Messrs. J. Hewitts & Son's Fireclay Works at Fenton Low, that, during excavation work for extension purposes, the workmen were unearthing teapot lids, etc., which, on examination, I decided were the products of Thos. Whieldon. The row of cottages adjacent

Fig. 1.—Supports used for Salt Glaze Ware.

to the excavation had always been known as Whieldon's cottages, the occupiers of which had found occasional pieces when working in their gardens. By permission of Mr. A. Hewitt, I visited the site on several occasions and gathered quite a miscellaneous collection. I, therefore, communicated with Major Frank Wedgwood, who at once recognised the importance of the "Pre Etruria Wedgwood." Since then, Messrs. Wedgwood and myself have carried on a systematic examination. The results, though fragmentary, and, as regards the finding of complete articles, somewhat disappointing, are of great interest, since they furnish

data as to the methods employed in the period under review.

With regard to raw materials, I am satisfied that Whieldon used flints, since I have discovered several boulder flints. This was to be expected, since the introduction of flints dated from 1720. Positive evidence, however, is to be found in the note book referred to previously. Through the courtesy of Mr. F. Lambert, the Curator, I have examined Whieldon's note book, and find that the flint grinder was paid six shillings per ton for grinding. He was expected to provide his own candles, and further, to call on his father to help when necessary. In connection with flint, one interesting point arises. It is stated that, in 1733, Shaw introduced "Bitstone" into pottery production, the material being bits of stoneware. Whieldon undoubtedly used Bitstone, which contained 85 per cent. of silica.

Fig. 2.—Supports used for Red and Black Ware.

The types of ware made by Whieldon were: (1) Slip decorated ware; (2) Salt glazed ware; (3) Black and red glazed ware; (4) Surface agate; (5) Solid agate; (6) Mottled glazed, and (7) that beautiful ware known as melon, pineapple and cauliflower. Mr. A. Hewitt possesses a good specimen of combed ware, and a number of fragments from my own collection are on view. Up to the present, I have not found any working utensils likely to have been used in this slip decorative process. Samples of "combed slip" ware dug up from reasonably dry portions were in

excellent condition. On the other hand, specimens from damp localities were crazed badly, the coloured engobe in some cases having peeled off from the underlying body.

Considerable quantities of fragments of salt glazed ware have been unearthed, together with a number of the usual type of perforated saggars. I would call special attention to the thickness of the walls and bottoms of the Whieldon saggars. A portion of one shows clearly the thickness of bitstone, etc., on the bottom. These saggars were thrown on the wheel as indicated on page 339. The silica content of the salt stoneware saggar was proved to be 68·5 per cent. and the refractoriness, Seger Cone 20.

A few weeks ago the slip kiln which had been used for the production of white clay was uncovered, the constructional details being very similar to modern drying kilns. The clay left in the brickwork was white and extremely tough, as was to be expected, considering the extended period of ageing. With regard to moulds, we have to some extent been fortunate, a portion of a pitcher case and of an alabaster mould (carved) having been found. It is unfortunate, however, that the latter was coroded to such an extent as to be unrecognisable. It is recorded that Aaron Wood, who was the best block cutter of the period, worked for Whieldon,

Fig. 3.—Prepared Agate Clay.

and that his workshop was kept locked to prevent any outside interference. Several plate profiles made of stoneware have been found. I would like you to note the initials and dates*. Large quantities of the placing supports used for his stoneware have been discovered. They appear to have been thrown on the wheel and afterwards cut to shape, the number of supporting projections ranging from three to six. The larger stoneware pieces were supported on rings built on the top of pillars. I have determined the silica content of the dinner plate and stoneware supports and found them to be 77·6 and 70·9 respectively. Whieldon appears to have

*It was the custom, when pitcher profiles, etc. were in use, for the Potter to scratch into the article his initial and date. The two plate profiles are marked C.D. 1762 and P.M. 1765, respectively.

manufactured scratch blue, and though these specimens are few in number, they are of great technical merit. It would appear that Whieldon experimented with lead glazes on his plates; in some cases the ornamental detail is destroyed by the glaze. Fragments of crucibles, evidently used for the production of the blue calyx, are also among the exhibits.

Abundant evidence is now available that Whieldon was an artist in the production of plain red, and red goods ornamented with white embossments. A large batch of prepared red clay was found at a depth of about six feet. It was in excellent condition; I have had several teapots thrown from it, the thrower stating that he had never worked such tough clay.

Whieldon red ware productions are of remarkable thinness, and judged by the presence (or absence) of wreathing, his throwers must have been very proficient. The handles were mainly of the

Fig. 4.—Teapot Lids of various Types.

familiar ""Crabstock" and plain types, though others appear to have been rolled and then pressed into moulds in order to impress upon them ornamentation, in some cases for their whole length. I make this statement with reserve, since it may be that expression boxes with pitcher dies were in use, though the use of them at this date has not been recorded. Regarding the raised ornamentation, I have made a very detailed examination of the pieces, with the object of determining whether the "sprigs" were made from moulds and then applied, or whether small pieces of clay had been arranged in the required position and then stamped. It is my

opinion that the latter process was used, as, on quite a number of pieces, the outline of the stamp can be clearly seen.

I am specially interested in several of the teapot lids and also a portion of a red teapot, which show that Whieldon was attempting to copy the "Elers" type of red stone ware. The surface and workmanship of these, however, are not up to the standard of those made by the famous Dutchmen or their immediate successors. The spouts indicate that the productions were of his later manufacture. The glazed teapot spout cases throw an interesting side light on the customs of those days, one of them being marked "One-dish." At that period the potters' indication of teapot capacity was one-dish—two dish, etc., instead of the modern 24-30-36, etc. It should be noted that the use of pitcher cases would give a product absolutely free from seams.

Fig. 5.—Fragments of Salt Glazed Plates, and Pitcher profiles used in their Production.

The specimens of black glazed ware are of very good technical quality and possess a "bloom" and brilliancy not surpassed by present day products. It has been stated in the literature relating to Whieldon that he produced his black glaze on a red body, by making additions of manganese, cobalt, etc., to his galena glaze. Most of the specimens unearthed at Fenton Low are a very dark chocolate, others being black bodies. It is difficult to state whether or not this dark colour is due to firing treatment. Examination under a lens (using a low magnification), does not

reveal any signs of bloating, which would have been expected if a reducing fire had been used to give the dark body.

An undated recipe in Whieldon's notebook reads: "Magnap 2 lbs., ochre 6 lbs., scales 2 lb., red clay 3 lbs, Tough Tom (a good old-fashioned term) 2 lb., white clay 4½ lbs. and flint ½ lb." This appears to be a mixture for a black body, and, I should imagine, one that would give good results. The black glazed cream jug is a real treasure, on account of the cracking which has taken place. These cracks wind round the jug in a spiral form and are clearly the result of bad throwing. I stated previously that Whieldon's throwers were experts, but the cream jug proves that even they were not perfect.

The saggars used by Whieldon for the glost firing of his red and black ware were unglazed. In any case, none of the specimens discovered at Fenton Low was glazed. The supports are worthy of close attention because they show ingenuity of design. The majority were obviously thrown on the wheel and the "pins" stuck on afterwards, a smaller number having been rolled out, joined, and then "pinned." A curious fact in connection with these Whieldon stilts is, that in many instances red rings had white points, white rings red points, and red rings black points. I cannot suggest any reasonable theory to explain this procedure.

Agate ware was one of Whieldon's staple lines, both slip and solid; excellent specimens, including biscuit and glazed knife hafts, have been secured. It is my opinion that some of the finest veined agate was produced from coloured slips mixed together, and allowed to stiffen sufficiently to be wedged. I found a large batch of marbled clay in a basin-like depression surrounded on the sides and underlain by ordinary red clay. This method is additional to the usual one of layering and wedging.

Every private collector of English pottery endeavoured to secure pieces of the important group of Whieldon ware in which the copper green glaze was used so extensively. The local and national museums are particularly rich in good specimens.

Mr. Harry Barnard has proved conclusively that Josiah Wedgwood, on March 23rd, 1759, produced a green glaze to be laid on common white (or cream) bisque ware. Wedgwood's comment—"very good"—was written while he was in partnership with Whieldon (Jewitt gives the date of the discovery as 1754). It is remarkable that, as yet, no fragments of copper-green glaze have come to light during our excavations. From a consideration of these facts, interesting and far reaching questions arise. Did Wedgwood realise the commercial possibilities of his discovery and decide to leave Whieldon and start on his own? If so it may be that many of the prized specimens are not Whieldon at all, but Wedgwood.

I recently discovered the foundations of one of the ovens. The diameter was 8 ft. 6 in., so that the oven proper would be a

relatively small one. It may be that other foundations will be found, since in his note book we have reference to men who worked at "Ye Huves." From a technical point of view the pitcher "contraction pyrometer," initialled by G.C. and dated 1762, is of prime importance. It indicates that the measurement of heat-work by means of contracting clay was in use almost twenty years before Josiah Wedgwood submitted his pyrometer to the Royal Society. One wonders whether this pyrometer, obviously used at the Whieldon pottery, had been introduced by Wedgwood during his partnership, the improved one finally adopted at his Etruria works being the result of further painstaking pioneer work.

Whieldon was a very cautious man, for Jewitt records that "to prevent his production being imitated in quality or shape, he always buried the broken articles." It is strange that their disinterment should provide modern potters with food for thought. It should be remembered that there is not a single Whieldon, or so called Whieldon, specimen extant which bears a distinguishing mark. It is true that there is a jug marked "Thomas Hammersley," who was milkman to Whieldon. Vague as this may be, it is the nearest approach to authenticity; hence the value of the fragmentary pieces recently excavated. At any rate we must agree with William Burton: "For the post of honour no name could enter into competition with that of Thomas Whieldon, who between 1740 and 1780, improved all the older processes and wrought with them new kinds of ware."

In conclusion, I wish to thank Messrs. J. Hewitt & Sons for their valuable help during the excavation.

DISCUSSION.

Mr. Barnard:—At present the whole question of the Whieldon pottery has to be developed. Mr. Emery has already referred to one of my statements on this subject, but I am still waiting to hear what others have to say. The investigations are not by any means completed. I think it probable that the history of the pre-Wedgwood period and the Whieldon period will have to be re-cast.

Mr. A. Heath:—Is the pyrometer of the contraction type, as we always understood Wedgwood was the originator of the pyrometer?

Mr. Emery:—Wedgwood had been associated with Whieldon prior to the date shown on the pyrometer.

Mr. Pape:—I have come to-night as a guest because I am extremely interested in the history of pot-works. I think that this Society might do a little more in the way of digging. Some years ago Mr. Emery came with me to do some digging at Bradwell Hall Farm to see if we could find the Elers' Oven, supposed to be

near an old barn; but the area which had to be dug out was considerable and so we could only make trial excavations. We did not find any Elers' ware, but we found evidence of old pottery made on the site. There was no proof that the Eler Brothers had possessed a pot-works at Bradwell House Inn. We have a lot to learn about the history of potters before 1800 and probably this can best be done by excavating.

XXX.—Dust Counting in the Pottery Industry with Special Reference to Health Considerations.

By E. L. Middleton, M.D., D.P.H.
(H.M. Medical Inspector of Factories.)

To appreciate the value of estimating the amount of dust in the atmosphere in an industrial process, and to understand the effect which exposure to the inhalation of dust may have on the individual, it is necessary to consider the structure of the human lung, and more especially that part of it which provides the natural protective mechanism against dusts which reach the air passages.

All the air which reaches the lungs in the processes of respiration passes through the nostrils and mouth, and from these it passes to the cavity of the pharynx and from this to the larynx, wind-pipe, and bronchial tubes.

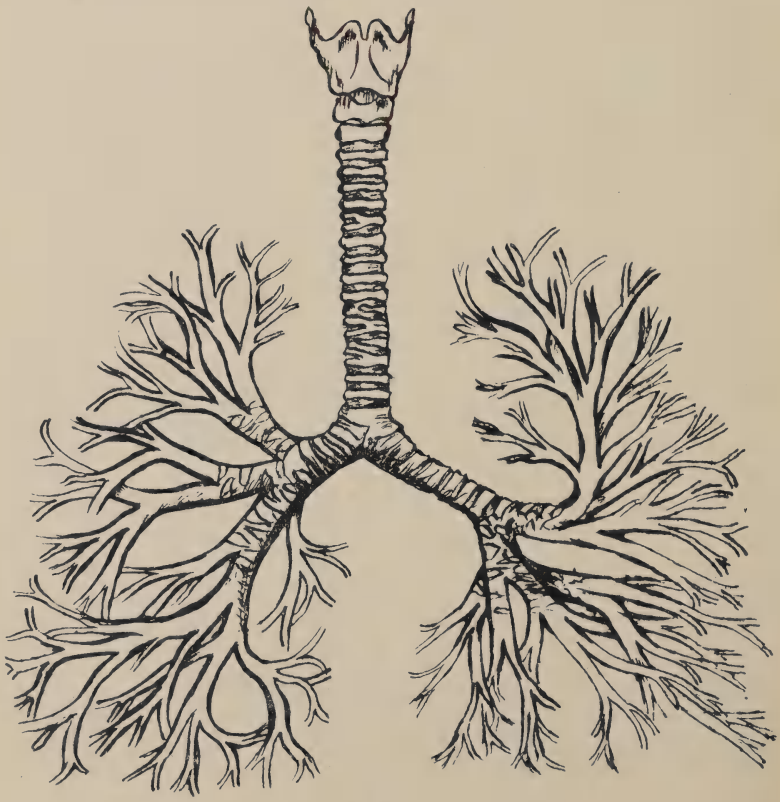

Fig. 1.

The bronchial tree. (Fig. 1). The trunk is represented by the windpipe or trachea, and the branches and twigs by the bronchial tubes, which by subdivision penetrate the farthest recesses of the lung. The leaves of this tree are represented by the air cells which are situated at the end of the finest bronchial twigs and these constitute the end organ of respiration—the ultimate lung tissue. The trunk, the branches and the twigs of this tree are hollow, and the air cells may be regarded as minute balloons (Fig. 2), opening off the alveolar passages which lead from the finest bronchial twigs. These balloons are closed except for the opening into the bronchial twig, and by an extensive system of dilatations and alcoves the air cells present an enormous surface, estimated by Zuntz at 90 square metres, to the action of the air which enters, and thereby enable rapid interchange of gases between the blood circulating behind the alveolar walls and the air in the cells.

Fig. 2.

The inner walls of the trachea and all the bronchial tubes are lined with a highly specialised kind of tissue—a mucous membrane—the surface of which is composed of cells provided with numerous fine processes called cilia, and forming a continuous covering over the whole surface of this lining membrane. The cilia have a remarkable property of keeping up a waving or sweeping motion, so that the mucus which is poured out on the surface of the mucous membrane from the glands under the surface is swept slowly, gradually and persistently in a direction towards the larger bronchial tubes, and on to the trachea, and can then be removed in the

expectoration. The mucus secreted in the manner described is a viscous, clear fluid which is perfectly adapted to the purpose of entangling dust particles and assisting in their removal, and also for protecting the delicate lining of the bronchial tubes from harmful action of larger sharp particles which reach the upper air passages.

The air cells. The lining membrance of the air cells and their passages (the balloons), is not provided with cilia, and when dust falls on this membrane another kind of protective mechanism is called into play. Living cells are separated off from the lining membrane so that they are able to move about, and similar cells derived from the tissue spaces outside of the air cells also find their way in through the walls of the air cells; and when dust particles fall on the surface of the delicate lining membrane a kind of irritation is produced which enables the free cells to locate and move towards the particles and then to engulf them in the substance of their own bodies. These free cells are called phagocytes and the process of taking up foreign particles is called phagocytosis. When one of these cells takes up as many particles as it is able to accommodate, it moves away either to the opening in the bronchial twig, in which case it is swept out by the action of the cilia and is removed in the expectoration, or it passes through the wall of the air cell and so into the lymph spaces of the lung. The objective is then the parts of the lung which are not urgently necessary for purposes of respiration, where the dust may be deposited without producing any serious effects, and the route is along the lymph vessels which everywhere drain the supporting tissue of the lung. When the amount of dust reaching the air cells is excessive, or is of such a kind as possesses specially injurious properties, the phagocytes, being overloaded or injured by the particles which they have ingested, fail to find their way through the lymph channels, and they, with their burden, become impacted in the channels and obstruct the passage of after-coming cells. Thus an accumulation of dead phagocytes results, and their contents are shed into the tissues. This result occurs, typically, in the case of silica dust. These cell-contents, the dust particles, act either as a foreign body or as a chemical poison, or in both ways, and around the accumulation there grows a ring of scar tissue which assumes the form of a nodule, at first very minute but increasing in size as long as excessive amounts of dust are inhaled and large numbers of phagocytes are intercepted in their way along the lymph channels. By such growth in all directions, the nodules tend to coalesce and by their encroaching on the air cells of the lung the functions of this organ are interfered with. Even after the inhalation of dust has ceased, new fibrous tissue continues to be formed, and the tendency of this newly formed tissue is to produce consolidation of the lung with consequent loss of res-

piratory capacity, and an increased liability to the supervention of tuberculosis.

The tidal air. During ordinary quiet breathing, the air which is inspired through the nose and mouth does not pass directly to the air cells, but flows into the reservoirs formed by the upper air passages. At the same time, with each inspiration, the air cells expand and become filled with air from the finer bronchial tubes. During each act of expiration, the reverse process occurs, the air cells are compressed, the air passes from them to the bronchial reservoir, and by and by it ebbs from the nose and mouth with the out-going tidal air.

The partial arrest of inspired air has a definite effect on suspended particles; they are damped, subjected to eddies which tend to produce aggregation into heavier masses, and, by the action of gravity and the force of the air currents, the larger particles and aggregates are thrown upon the walls of the air passages, and, becoming entangled in the mucus, are finally removed by the outgoing current established by the cilia. It is, therefore, only the finest particles which, by remaining in the central air current, can avoid being retained by the viscid mucus covering the bronchial tubes and so reach the cavity of the alveolar passages and the air cells. Here they may be arrested to be removed by the phagocytes, or they may, by remaining free, recede with the outgoing tide of the next expiration.

The dust particles. Two classes of dust particles can be distinguished in relation to the phenomena described: (1) those which can reach the alveolar spaces in the ultimate lung tissue; and (2) those which are arrested in the upper air passages. The first class includes very fine particles, which are capable of remaining discrete in spite of the damping and precipitating effect of the conditions met with during their progress through the upper air passages and the whole length of the bronchial tubes; while the second class comprises all the coarser dusts and those which readily form aggregates under the conditions described.

Of these two classes, the first, the fine, discrete dust is by far the more important from the point of view of the effect on health, and of the fine dusts which occur in industry the most destructive is silica in the form of flint or quartz, the action of which on the lung has already been described. The particles of silica found in the lungs of persons who have suffered from the form of fibrosis of the lung known as silicosis, are all of very small size, the largest being about 10μ ($1\mu = \frac{1}{1000}$th millimetre or $\frac{1}{2500}$th inch), the great majority being round about 1μ in size. From this it may be deduced that only particles under 10μ in size are important in the causation of silicosis. Larger particles do not reach the air cells, but are caught in the upper air passages or the bronchial tubes. It is important, therefore, in estimating the amount of dust in the atmosphere, to determine the size of the particles.

Methods of estimating atmospheric dust. There are three methods of estimating the amount of dust in the atmosphere:—

1. Colorimetric—used for estimating smoke, etc., by comparison of the depth of stain produced on a filtering fabric by the passage through it of a given volume of air, with standard stains;
2. Gravimetric—in which a measured volume of air is passed through a retaining medium such as sugar, filter paper, or water; and the dust collected is weighed and the result expressed in milligrammes per cubic metre of air.
3. Enumeration—in which a small sample of air is made to impinge at high velocity on a microscope slide, and the deposited dust is subsequently examined and counted under the microscope.

The value of dust determinations. All forms of atmospheric dust estimation must be regarded as having only a relative value, because of the limitations inherent in the method. For example, the amount of dust obtained by any of these methods represents that amount, or a portion of it, which was suspended in a certain sample of air at a given time, that is, first, the sample is purely local and can only be assumed to resemble what occurs in other places; and, second, the sample is limited to a comparatively short space of time and again can only be assumed to represent what occurs at other times.

These considerations are important, and in assessing the value of dust determinations by sampling they must not be lost sight of. At the same time, the results so obtained represent facts, and by repetition and accumulation they form a chain of evidence which it is impossible to gainsay. Another objection to which all the methods are open, is that the most perfect instrument does not retain all the dust from the volume of air which it represents. On the other hand, it is never really necessary to ascertain the precise weight of material or actual number of particles in a given volume of air, since it cannot be proved how much is actually retained in the lungs or is an effectively deleterious agent. What does matter, rather, is the comparative degree of air-dustiness comparing this set of conditions with that, *e.g.*, comparing outside air with workroom air, under comparable conditions of sampling. To such data we must apply another set of data which have been derived from experience in other ways—which conditions have proved to be compatible with continued health, and which have been associated, time and again, with a consistent picture of injured health.

The two kinds of data are complementary to each other, and it is by the accumulation of both classes of data, accurately derived and carefully compared, that useful conclusions will be

reached as to the safety line which must be attained before healthful conditions can be assured.

The choice of a method of dust estimation will depend upon the object in view; this, in turn, is largely determined by the nature of the dust under investigation. For example, in the case of lead dust, which, when inhaled, acts as a poison by the eventual solution of the lead taken into the lungs, a gravimetric method is most convenient, for in this way the amount of lead can be determined by weight which a worker is liable to inhale and absorb in the course of a working day. According to Legge, if a quantity exceeding 2 milligrammes per day is absorbed, the conditions are sure to produce lead poisoning.

The size of the particles. In the case of silica dust, the important consideration is the amount of dust which will reach the air cells of the lung and be liable to be deposited in the lung tissues so as to produce the form of fibrosis known as silicosis. In this case, the fine particles being most important, any method which includes large particles in the resulting estimate will be misleading, since a single particle of 100 microns in size weighs the same as many thousands of particles of 1 micron, but in respect of the causation of silicosis a particle of 100 microns is of no importance, while each particle of 1 micron is potentially injurious. It is possible by means of calculation to arrive at an approximate estimate of the number of particles of different sizes in a given weight of a known substance, and in this way a gravimetric method might be used for enumeration; but, for practical purposes, the direct method of enumeration with the use of a konimeter is to be preferred as the simplest, quickest, and most convenient for field work.

In the South African Gold Mines, a konimeter invented by Sir Robert Kotzé, is used for estimating the conditions in the mines. In this instrument the record is a circular spot, which can be examined under a low power of the microscope with sufficient accuracy to provide an index of the dust conditions in the mine, and to demonstrate to the practised observer the efficiency or otherwise of the dust-controlling provisions. The conditions in and about those mines are particularly favourable to this kind of dust sampling, since the processes are comparable throughout, and by taking very large numbers of samples as a routine procedure, the relative values can be compared with a set of standards.

In research work, however, and in industries where many kinds of dust may be produced in many different processes, any observations of atmospheric dust must be made in detail, the values of each sample being assessed on a basis of observation as accurate as the circumstances permit. There are no set criteria to form a basis of comparison, and before the stage can be reached when a rule-of-thumb method can be applied, much close application must be given to the examination of the constituent dusts

and their relative and absolute importance from a health point of view.

Dusts of extraneous origin. An important point is the presence in the atmosphere of industrial towns of extraneous particles, the most prevalent of which is smoke. The presence of these particles constitutes perhaps the most serious drawback to the use of the konimeter and the counting method. Much may be done by taking control samples in places representative of the ordinary atmosphere of the locality, to enable the observer to allow for the extraneous particles, but the problem is not quite so simple, and to the beginner strange anomalies appear. It is only by practice and experience that these can be fully understood, and while it is impossible to give even an indication of the difficulties, one example may be permitted: In a workroom in which a dusty process is being carried on, the dust count may prove to be lower than one taken in the open air close by, with no evidence of any source of dust: the reason is that particles of smoke, etc., remain free to a greater extent in the open air than in workrooms where changes of temperature, draughts, moving machinery, humidity, and so on, produce clumping of the particles; and, moreover, coarse particles of dust given off from an industrial process seem to have the power of attracting to themselves smaller particles of smoke and other dust which may be present in the atmosphere. These factors, by producing aggregation of small particles, reduce the count indoors, and, while to the careful observer the records are quite different in appearance, a mere enumeration of particles will convey very little to the uninitiated in a written report.

Again must be emphasised the importance of practice, experience, and the accumulation of accurate observations.

Dr. Owens' Apparatus for Dust Examination.

Principle.

This apparatus depends for its action on the following principle:

When air which contains dust passes through a narrow orifice towards a glass surface, which faces the jet a short distance away, the dust will adhere to the glass and can be examined microscopically.

In the instrument this result is brought about by causing a very fine, ribbon-shaped jet of air to strike a microscope cover glass placed about 1 mm. from a slot-shaped opening forming the jet. The air before entering the slot passes through a damping chamber, and the velocity in the jet is such that a fall of pressure results, thus bringing about a condensation of moisture. The air is then deflected and the dust, being unable to turn the corner, strikes the cover glass, the velocity of the air falls off, the pressure and temperature rise, causing the water to be evaporated, and the dust is left behind.

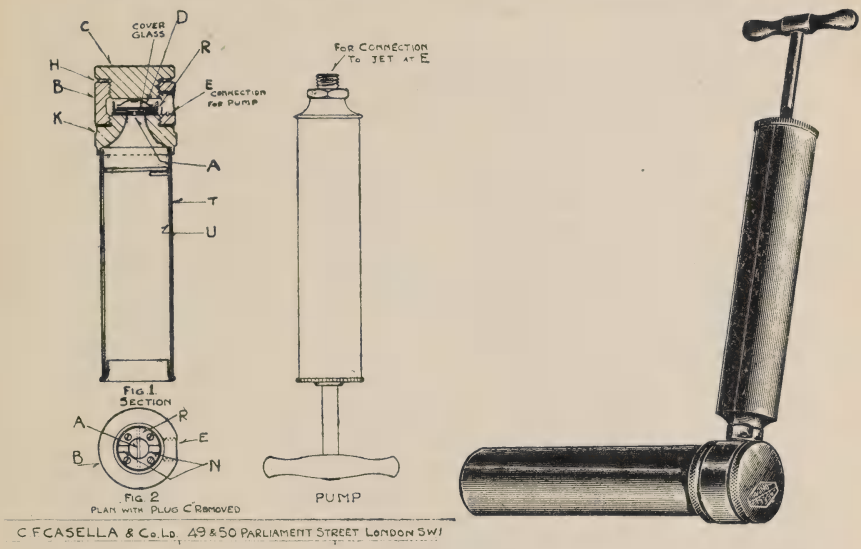

Fig. 3.

Description.

Referring to Fig. 3, the apparatus consists of a brass sleeve *B* open at the top and bottom and screwed internally for the reception of a piece *K*, which latter is perforated by a central hole for admitting the air to a narrow slot formed diametrically across the hole by means of two semi-circular metallic plates held in position by a ring *R* attached to the plug *K*. The upper surface of this ring is recessed to form a bed for a microscope cover glass, and a central cell 10 mm. in diameter and 1 mm. deep is formed under this cover glass. In the floor of this cell is the narrow slot for forming the jet.

Into the upper opening of the sleeve *B* fits a screwed plug *C*, on the inner end of which is fixed a three-claw spring, by which the cover glass is held gently down on its bed when the plug is screwed home. The washer *H* makes an air-tight joint between the plug *C* and the sleeve *B*. Inside the sleeve *B* and surrounding the cover glass is an annular recess which communicates with a connexion *E* for attachment to a 50 cc. air pump. Channels *N* are formed on the upper surface of the ring *R* under the cover glass, as in Fig. 2, so that when air is drawn from the space between the plugs *C* and *K* by the air pump, a jet of air enters the slot *A*, impinges upon the cover glass and escapes to the annular space in *B* and so to the pump *E*.

A damping chamber *T* is provided, which is detachable from the plug *K* by unscrewing and this is lined with blotting paper, which is wetted before the instrument is used.

Instructions for Use.

To take a record the pump is fixed to the connexion E, and before the plug C is removed three or four strokes of the pump are made to fill the damping chamber with the air to be tested, leaving the pump plunger pushed in. The plug C is then removed rapidly and a carefully cleaned cover glass placed in position upon the ring R, after which the plug C is replaced rapidly and screwed home. The pump plunger is then pulled out *smartly* so as to draw one or more volumes of air through the jet, allowing an interval of about one-quarter of a minute between each pump stroke to permit the air to absorb moisture from the damping chamber. The plug C is then removed and the cover glass dropped out on to the hand and mounted on a microscope slip. Suitably prepared slips are provided having metallic rings dressed with an adhesive material to which the cover glass adheres. The record may then be placed under the microscope for examination.

Examining Records.

It is advisable to use a 1 inch (25 mm.) or $\frac{2}{3}$ inch (16 mm.) objective for finding the record with the aid of a dark ground illumination, which latter can be obtained simply by inserting a suitable stop under the substage condenser.

A $\frac{1}{6}$ inch (4 mm.) and $\frac{1}{12}$ inch (2 mm.) oil immersion are the most suitable for further examination. If a rough count of large particles is required the $\frac{1}{6}$ inch will do, but for more accurate counting the $\frac{1}{12}$ inch is essential.

Counting.

An eye-piece should be provided having in it a net-ruled micrometer, of about 1 mm. squares, to facilitate counting.

The record consists of a linear deposit of dust, and a count of the number of particles in this may be made by the aid of the eye-piece micrometer, a strip one square wide being counted completely across the record at one or two places, and an average taken. This figure multiplied into a factor, depending upon the magnification used, will give the number of dust particles on the record. To ascertain the factor, the number of such strips in the length of the record may first be counted under a low power. Supposing $\frac{2}{3}$ inch objective is used for counting and there are fifty strips in the length of the record; then, if the $\frac{1}{6}$ inch magnifies four times as much as the $\frac{2}{3}$ inch, the number of strips, when using the $\frac{1}{6}$ inch, will be 200. If the $\frac{1}{12}$ inch magnifies ten times as much as the $\frac{2}{3}$ inch the number of strips will be 500, when examined under the $\frac{1}{12}$ inch. Supposing that in a particular case 300 particles are found in a strip across the record when examined under the $\frac{1}{12}$ inch, and that 50 cc. of air have been drawn through the jet, the number of particles per cc. will be:—

$$\frac{300 \times 500}{50} = 3000$$

Generally, if:—

S represents number of strips in the length of the record,
N represents the number of particles per strip,
C represents the number of cc. drawn through the jet in taking the record,

then:—

$$\text{Number of particles per cc. of air} = \frac{N \times S}{C}$$

To simplify matters it will be advisable to use the same volume of air for each record, as far as possible, and to count under the same objective and eye-piece.

Thus the factor $\frac{S}{C}$ will remain constant.

A microscope with mechanical stage is the most suitable for counting, as it permits the record to be moved slowly across the field.

When a high power is used, it is necessary before counting to decide the smallest particles to be included in the count. Very small particles down to about 0·2 micron will be visible but not completely resolved, and, in practice, it is well to fix a limit beforehand, say 0·3 or 0·5 micron, which practice will make sufficiently readily distinguishable.

Dust control measurement. One of the most important practical applications of atmospheric dust determinations is the measurement of dust control methods. These include all the means adopted for keeping the atmosphere of the workplace free from excessive amounts of dust, whether structural design of the premises and plant, arrangement of the work, general and localised ventilation, or any other means directed to that end. A series of dust determinations taken from time to time at the same point in a given factory would provide a valuable index of the success or failure of schemes directed to the improvement of dust control.

The use of locally applied exhaust draught as near as possible to the point of origin of the dust is one of the most useful methods of dust control, provided that it is intelligently designed and used. This method depends for its success on the efficiency of the extracting force, usually a fan, the integrity of the duct system, and the arrangement of the openings in relation to the sources of the dust which it is desired to remove. The fan power which is available at the duct openings can be measured in terms of velocity of air current by means of the anemometer. A simple type of instrument which gives a direct reading on the dial in linear feet per minute is generally convenient. The velocity so obtained can be converted into cubic feet of air moved through each duct opening, by multiplying the area of the opening in feet by the velocity in linear feet per minute. The air extracted through

such a duct is derived from every direction of access to the opening, not only in front of it but from the sides and above and below, so that much of the air removed is not in the line of the source of origin of the dust, unless means are taken to shut off these useless lines of access to the duct opening, and, as far as possible, to create a directional air current from the breathing level of the worker through the dust source to the duct opening. This is ideal, and can only be approached in practice, in a process requiring free movement of the worker, such as the placing of china biscuit ware, but if the principle be kept in view it may be possible, by arrangement of the work and the use of baffle boards, to cut off side currents and get the best value for the power available in the exhaust system.

The maintenance of an efficient system of general ventilation is an essential for the success of a localised exhaust system, and it follows that the inlet openings must be so arranged as to provide a flow of pure air in a direction from the worker towards the openings in the exhaust ducts. It follows also that no process must be carried on in any part of the room so as to give rise to dust which will be carried past the worker towards the exhaust duct openings ; in other words, the air at the breathing level of the worker should not be vitiated before it reaches him.

Other considerations. The methods of dust control which are independent of the worker are likely to yield more uniformly successful results than those which depend upon the human factor. The latter include the wearing of respirators, care in manipulation of dust and dusty objects, damping of flint at the bench, and so on. While these will afford some protection to the individual worker, too often the careful worker is at the mercy of a careless mate.

From the brief outline which it has been possible to give here, it is evident that the remedy of the dust evil in the Pottery Industry lies in the industry itself. By the investigation of all the available systems of dust control, the adoption of the best of these, and the intelligent and loyal co-operation of all concerned in seeking to attain safe working conditions, the Pottery Industry can be made safe from the dangers of the inhalation of silica dust.

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DISCUSSION.

Dr. J. W. Mellor: How do you identify the dusts? I think the particles are too small to be identified by the usual tests: polarized light, and indices of refraction.

Dr. Middleton: The contention is quite sound. While it is possible, by petrographic methods, to distinguish one dust from another if the particles be of reasonable size, say over 2 microns, in practice this has only a limited application. For example, it usually happens that the important ingredient of a mixed dust is known, and, when such is the case, it is sometimes possible to distinguish particles of this dust, if its characters be sufficiently distinctive, from the other ingredients either by form, refractive appearances, colour or arrangement. In this way it is possible to give a rough estimate of the proportion of particles of flint, for example, on a record in which it is mixed only with smoke or even with clayey matter. Practice will enable the observer to associate certain dusts with their own characteristics.

Dr. J. W. Mellor: I assume that the proportions of the dust particles collected is a minimum value. Is there any evidence that the air that has been through the dust chambers has been tested again to find what dust passes through without being arrested?

Dr. Middleton:—The dust record is, it is true, a minimum value, that is to say, something less than 100 per cent. of the dust content of the given volume of air is stated in the count. But, as far as the efficiency of the instrument is concerned, the percentage accuracy is very high. Dr. Owens, the inventor of the instrument, experimented with a second cell, so arranged as to trap dust which passed the cover-slip interposed to form the record. He told me that the amount which passed was negligible for practical purposes, so that he abandoned the use of a second cell as unnecessary.

Mr. J. Burton:—Is there a particle so fine as to be practically harmless?

Dr. Middleton:—I am glad that this point has been raised, although, so far as silica dust is concerned, it really involves a highly controversial point which I purposely avoided in the lecture. On this question depends the wider one of "How does silica produce its harmful action on the lung tissue?" If this action be dependent upon the solution of the silica, then, it seems

obvious, that the finer the state of division the greater would be the amount dissolved and the greater also the consequent damage of the tissues. Other methods of action have been regarded as possible, for example the action of a foreign body producing irritation, or an action dependent upon change of the silica to a colloidal form; or again, a biochemical action following inclusion of silicon in the protoplasmic molecule of certain cells. We remember that the particles are taken up by phagocytic cells and carried off, and it is the failure of these cells, or some of them, that is, at least partly, responsible for the disorganisation of the functions of the lung. Now, if all the particles were so minute that no phagocytes failed by the way, it is conceivable that the lungs might be kept clear, but a proportion of larger particles will upset the balance and the minute particles also will be shed into the lung and, it seems to me, will augment the action of the less minute particles. Until these various hypotheses have beeu established or set aside, and the nature of the action of silica has been defined, it is impossible to place a limit on the size of the silica particles below which they cease to be harmful. In a very interesting monograph on the subject, Dr. Mavrogordato, working in South Africa, concludes that "phthisis-producing dust is the dust of free silica, of from one quarter to five microns in diameter." So far as practical dust-counting is concerned, the lower limit of size of particles to be included in the count, lies somewhere about 0·3 micron. In the case of soluble dusts which act as poisons, for example, lead, the finer the state of division when inhaled, the more rapid are the absorption and the appearance of symptons of poisoning.

SIR THOMAS LEGGE:—Are all the particles that we can see floating in the air above 2 microms ?

DR. MIDDLETON:—One of the important facts which the use of the dust counter will establish is, that the visual appearance of an atmosphere is no criterion of its freedom from a dangerous degree of dustiness. It has happened in my experience that an atmosphere apparently free from dust, even in bright sunlight, has been found to be charged with particles of silica amounting to over 4,000 in a cubic centimetre, and reaching up to 4 microns in size. It seems probable, therefore, that dust is invisible in the atmosphere when the particles are less than about 2 microns in size, unless the particles are present in sufficient numbers to produce a light effect. Clouds of smoke and other fine particles are revealed by the presence of relatively large aggregates or clumps. With deficient illumination indoors, fairly dense dust clouds may be invisible. On the other hand, a visible cloud of dust given off in an industrial process has been found to give a relatively low count, consisting almost entirely of large aggregates.

XXXI.—Refractories for Gas Retorts, with Special Reference to Silica.*

By W. Emery.

INTRODUCTION.

AMONG the mass of detail published on the subject of silica refractories, little can be found which is of any help to the hard-worked provincial gas engineer, who may be faced with the necessity of reconstructing his plant, and who wishes to advise his committee or his directors as to the refractory which will prove to be the most efficient and economical when adopted at his station.

I have had the privilege, through the kindness of many members of the Gas Institution and of many of the large gas engineering contractors, of obtaining information from a number of installations in this country where silica retorts are in use, and I propose to discuss some of the points and problems which have interested me during the investigations.

It is convenient to adopt the official classification of the Gas Institution in referring to refractory materials; this classification describes as siliceous those materials in which the percentage of silica lies between 80 and 92, and as silica, those materials having a silica-content exceeding 92 per cent. Since vertical retort practice is definitely pledged to the use of silica or highly siliceous refractories, it will be more useful to members, whose aim is the impartial investigation of the properties of this material as a factor in engineering construction, to focus attention upon horizontal practice, and to see how the adoption of silica has advanced this type of plant.

The following claims have been made for and against silica materials:—

Advantages.

Increased rate of carbonization and throughput.
Longer life.
Rigidity and shape retained at high temperatures.
Heavier charges possible.
Resistance to abrasion.
Easily scurfed.
Not affected by ash in producer gas.
Less cracking.
Greater resistance to corrosion from salty coals.

Disadvantages.

Excessive expansion.
Special precautions required during setting.
Wear and tear due to alternations of temperature; spalling troubles.

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Deterioration when shut down.
Fragility and tendency to disintegration.
Life under varying working conditions not established.
Capital outlay.

The available laboratory data relating to the various refractories referred to in the report are summarised in Tables I.-II.

TABLE I.

	A1	A2	A3	A6	A7*
SiO_2	95·13	95·26	94·98	95·64	—
TiO_2	0·11	0·02	0·24	0·25	—
Al_2O_3	1·46	1·45	2·10	1·43	—
Fe_2O_3	0·43	0·42	0·70	0·68	—
MgO	—	0·23	0·10	0·08	—
CaO	2·55	1·61	1·72	1·50	—
K_2O	0·15	0·30	0·47	0·12	—
Na_2O	0·11	0·23	0·10	0·34	—
Loss	0·18	0·20	0·05	0·16	
*Manufacturers will not release analysis for publication.					
True Sp. Gr.	2·37	2·43	2·44	2·37	2·34
Porosity	39·24	30·46	34·84	29·54	28·20
App. Sp. Gr.	1·44	1·60	1·59	1·67	1·68
Aft. Expans.	0·20	0·13	0·25	0·05	0·07
(2) True Sp. Gr. ..	2·35	2·40	2·42	2·36	2·32

(2) True Specific Gravities, carried out on the same test pieces after they had been subjected to the "after-expansion" test.

TABLE II.

	B1	B2	B3	B4	B5	B6B*	B6R*	B7*	B8
SiO_2 ..	88·70	84·46	90·08	74·40	81·60	84·2	86·31	75·5	81·80
TiO_2 ..	0·86	0·86	0·40	0·60	0·70	—	—	—	0·62
Al_2O_3 ..	8·35	11·35	6·26	21·50	15·01	—	—	—	14·51
Fe_2O_3 ..	0·81	0·80	1·87	2·50	1·80	—	—	—	1·60
MgO ..	0·10	trace	0·05	trace	0·30	—	—	—	0·29
CaO ..	0·31	0·54	0·33	trace	0·20	—	—	—	0·85
K_2O ..	0·56	0·78	0·60	0·60	} 0·80	—	—	—	0·38
Na_2O ..	0·33	0·63	0·40	0·50					0·23
Loss ..	0·21	0·20	0·11	0·10	—	—	—	—	0·18
*Analysis relating to B6 and B7 not released for publication.									
True Sp Gr.	2·50	2·50	2·47	2·67	2·58	2·59	2·52	2·55	2·62
Porosity ..	31·20	33·20	32·80	27·76	30·50	28·60	25·80	22·90	32·83
App. Sp. Gr.	1·72	1·67	1·66	1·93	1·79	1·85	1·87	1·96	1·76
Aft. Expans.	0·45	0·26	0·22	—	nil.	0·12	0·31	—	—
Aft. Contra.	—	—	—	—	—	—	—	0·37	0·16

ADVANTAGES.

Carbonization and Throughput.—There is no doubt that silica retorts are very conducive to rapid carbonizing periods at high temperatures. This speeding-up has been mainly accounted for in terms of conductivity.

Conductivity.—The problem of the transmission of heat by way of the walls of refractory materials, *i.e.*, silica and fireclay retorts, is of primary importance to those engaged in the carbonizing industries. Unfortunately, the accumulation of data concerning this problem, obtained both from the laboratory and from the works, has brought much confusion and controversy. Although it is not my object to add to the controversial aspect of the subject, I should like to indicate certain facts bearing on the subject which may form the basis of a compromise between some very divergent points of view.

The statement that "silica refractories have a much higher thermal conductivity than fireclay refractories" has made a wide appeal to gas engineers and managers. Some of the advertisements issued by interested firms are written very ambiguously; others give such a definite opinion as to suggest that this problem of heat transmission is finally settled, and that the results can be encompassed in a single, most simple sentence. One particular circular contains the following statement: "Silica material has approximately 16 per cent. higher conductivity than fireclay at 1,000°." Unfortunately, gas engineers, who are always striving for increased thermal efficiency, are likely to be impressed by such definite expressions of "fact."

The published data concerning the thermal conductivity of refractory materials do not reveal any striking differences in the values for silica and fireclay up to 1,000°. There is, however, one notable exception, published by Professor Cobb[1], in which he reports a marked increase of diffusivity of silica as compared with fireclay at the temperature previously mentioned. Middleton[2] expresses doubts about the supposed higher values of silica at 1,000° but states that at higher temperatures its conductivity becomes considerably greater. In other words, in carbonizing plants where relatively low temperatures are employed, there is little to choose between silica and fireclay material on the ground of thermal conductivity alone. In an extension of his work on conductivity, Green[3] notes that the rate of thermal conductivity and diffusivity with temperatures in the neighbourhood of 1,200° is somewhat greater in the case of three well-burned silica bricks than in the case of an average of fireclay materials. His results are important, inasmuch as they suggest a confirmation of the works' results previously quoted.

It is essential to have a clear conception of what is implied by the term "thermal conductivity" in order to appreciate the commercial value of the data submitted by various workers. This aspect of the problem has been dealt with somewhat fully

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1 Dougill, Hodsman and Cobb, *Soc. Chem. Ind.*, **34**, 465, 1915.
2 Middleton, TRANS., **22**, 173, 1923.
3 Green, Private communication.

by Green[4]. Since it is material to the development of the present argument, I must recapitulate some of the more salient features of the above paper.

Consider the formula:—

$$K = kcs,$$

where K is the coefficient of thermal conductivity at a temperature of $\theta°$,

k is the coefficient diffusivity at a temperature of $\theta°$.

c is the apparent specific gravity.

s is the specific heat at a temperature of $\theta°$.

Such a formula can be used as the basis of comparison of the thermal conductivity of silica and fireclay. The product cs. may be called the heat capacity per unit volume of the material. The experimental evidence of Bradshaw and Emery[5] shows that the specific heat of silica is almost identical with that of fireclay up to temperatures of 1,400°.

This fact shows that the apparent specific gravity of silica or fireclay material is a direct measure of the heat capacity. The apparent specific gravity of silica material is almost invariably less than that of fireclay material (*e.g.*, 1·63 for silica and 1·95 for fireclay material), so that the heat capacity per unit volume of silica is less than that of fireclay.

"Diffusivity" or "temperature conductivity" is essentially concerned with rate of rise of temperature, and, in consequence, it gives some definite criteria for those heating units, such as gas retorts, in which the rate of rise of temperature is of more importance than the total heat-work effect. The coefficient of diffusivity may be defined as the rise of temperature produced in 1 cc. of the substance by one calorie in one second through one sq. cm. of a layer one cm. thick, having a temperature difference of 1° between the two faces.

To illustrate the significance of this conception, I may be allowed to quote an interesting experiment by Professor Tyndall. He showed that a temperature wave travels more quickly in bismuth than in iron, although the thermal conductivity of the latter is nearly six times greater than that of the former. The application of this conception to our study is illuminating. There is little difference between the diffusivities of silica and fireclay materials below 1,000°, although the evidence previously mentioned indicates that the diffusivity at the higher temperatures of practice is somewhat greater in the case of silica bricks. Herein may lie the clue to the opinion of many engaged in this industry concerning the problem under review.

As has been previously indicated, the thermal conductivity at a specific temperature is determined by the product of the heat capacity and diffusivity. Since the heat capacity of silica is lower

4 Green, TRANS., **21**, 394, 1922; *Trans. Inst. Gas. Eng.*, 1921-2, p. 195.
5 Bradshaw and Emery TRANS., **19**, 88, 1920; *Trans. Inst. Gas Eng.*, 1919-20, p. 101.

than firebrick, the diffusivity of the former must be much greater in order to obtain identical conductivities. Below 1,000° this increase in diffusivity is not generally noted, which leads me to believe that, in general, firebrick is probably the better conductor of heat at lower temperatures.

In a paper (TRANS., **23**, 253, 1924), on the influence of texture on heat transmission, A. T. Green suggests that the variations are primarily due to the disposition, size and orientation of the pores within the refractories. Further, it is suggested that greater values of increase in the transmission of heat are to be expected at high temperatures, together with the property of greater permeability to gases. The suggestion has an interesting bearing on the comparison between silica and fireclay materials.

I have examined a large number of refractories of all types after they have been used in commercial heating units, and I conclude, as a result, that there is less alteration in the porosity of silica goods (see Table) during use in gas installations than is the case with fireclay materials.

A. J. Dale (TRANS., **24**, 170, 1925), has studied the question not from a heat transfer point of view, but in connection with the refractory-under-load test. He states that the orientation of the pores in refractories is considerably modified when subjected to load between 1,300° and 1,400°. He has examined fireclay refractories, which show decrease in porosity ranging from 4 per cent. to over 15 per cent., whereas in no case do 95 per cent. silica refractories show marked decrease in porosity. I would suggest that the maintenance of porosity, while the refractories are in actual use, is a factor requiring very close attention.

I have on view representative samples of the retort material now available for gas works. The polished surfaces of these bricks show clearly marked differences in texture. For example, compare A7 and A1. The porosities of these are 28·71 and 39·24 respectively. Sample A6, which occupies an intermediate position between A7 and A1, possesses a porosity of 29·54. The manufacture of silica goods has, however, undergone a decided improvement. At an early period the texture of the goods delivered to gas works was of that general type which had given good results in metallurgical operations, but in many cases the firing of these goods was far from satisfactory. At the present time, the average grain size is less, the mass is much more homogeneous, and the firing more satisfactory. It is clear, then, that the makers realise the importance of texture and firing conditions as at least equal to that of chemical composition.

W. B. Leech[6] has pointed out how difficult it is, under working conditions, to assess the relative conductivities of refractories. He has assembled considerable data concerning the

6 Leech, *Trans. Inst. Gas Eng.*, 304, 1922.

internal and external temperatures of a great number of retorts, and, as a consequence, asserts that the use of silica retorts increases the internal temperature 60°, where the combustion chamber temperatures are in the neighbourhood of 1,400°. If it is assumed that (1) the chamber temperature remains constant and (2) the same amount of heat is passing through the retort in the two cases, *i.e.*, silica and firebrick material, it means that the conductivity of the silica in these circumstances is 30 per cent. greater than that of the firebrick.

With the exception of this case, I have been unable to obtain any reliable data on the internal temperatures prevailing in horizontal retort practice. I can appreciate the diffidence displayed by various engineers in passing on for publication any information regarding conductivity. However, since it may be that the next development in large town gas installations will be the adoption of chamber practice, the observations and data published by Middleton, Townend, Hebden and others will be applicable to the gas industry. I have elicited one or two interesting facts having a distinct bearing on the present arrangement. Mr. Thompson, of Messrs. Drakes Ltd., who has had a unique experience with the use of silica retorts, reports that, in his opinion, working heats may be obtained more rapidly in new silica retorts than in new fireclay retorts.

The following incident occurred at a Northern Gas Works. A setting of silica retort material had been installed, and whilst the heats were being raised, several of the "lungs" gave way, with the result that the normal working temperature could not be attained. This occurred during the "peak-load" period and, consequently, the setting had to be worked. The management were definite in their opinion that it would have been very difficult in like circumstances to have carbonized in fireclay retorts, and they estimated that, even if it had been possible, a further four hours would have been necessary.

It is clear that the increased carbonizing temperatures now prevailing must lead to an increased carbon deposit. Nicholson[7] and Warner[8] have already discussed this problem, dealing with the effect on porosity. Laboratory data are lacking as to the behaviour of carbon in the pores, but Cobb[9] has stated that, in his opinion, the infiltration of carbon into the pores results in increased thermal conductivity.

The following data have been obtained concerning the scurf deposit taken from a gas retort, and may be of interest in connection with the effect of this scurf on heat transmission:—

True sp. gr.	App. sp. gr.	Porosity.
2·12	1·78	16·0

7 Nicholson, *Gas World*, **80**, 14 C.S., 1924.
8 Warren, *Gas World*, **78**, 183, 1923.
9 Cobb, *Loc. cit.*

In assessing the relative thermal efficiency of silica material, the fact that the general adoption of more completely filled retorts and higher temperatures has more or less coincided with the extended use of silica retorts, must not be overlooked.

A summary of the available data suggests that the heat transfer will be more rapid in silica at the high temperatures now in use, *e.g.*, 1,350° to 1,450°. Evans, in his recent series of lectures, has shown that the temperature prevailing in the interior of retorts during the initial period after charging is all important. If the assumption be valid, that the diffusivity and thermal conductivity of silica are higher than those of fireclay, then it is obvious that the first named refractory will give better results. It must be remembered that the infiltration of carbon into the pores of the material will invalidate any laboratory measurements on the conductivity of the "pure" refractory.

It is interesting to note that the constructional engineers, who are responsible for the modern vertical installation, do not suggest that increased thermal conductivity is obtained by the use of silica constructions; rather do they stress that improvements may be looked for owing to the increased stability at high temperatures.

Longer Life.—The life of the retort is a factor which is of great interest to the gas engineer. A long life means lower capital charges, a considerable reduction in carbonizing costs, whilst in the provincial works the engineer is not always faced with the worry of calling in contractors and engaging bricklayers for the purpose of renewals. It is natural, considering that the utility of silica retorts has only been realised during the last ten years, that reliable data relating to the life of such constructions used in town gas installations are somewhat meagre. Fortunately, for the industry at large, Mr. Leech and his staff at Beckton, have carried out very extensive works' research with silica settings, and their published results have set a standard of comparison for the industry. Other gas managers and engineers have made extended trials with a similar material, but at present, the full results are not yet available for publication.

R. G. Shadbolt states that silica retorts have a life at least one-third longer than moulded fireclay in plants where hand stoking is adopted.

The following data relating to retorts other than silica are included, so that one can judge of the life of modern fireclay and siliceous materials compared with that obtained by the Beckton methods.

Mr. Firth[10] has already communicated a note relating to the use of siliceous and silica retorts, and, in reply to a letter from me, states that the siliceous retorts which he uses are built up of three segments. The retorts are in very good condition after gas-making for 219 days, during which period 263 tons of rough slack per retort

10 Firth, *Gas J.*, **165**, 641, 1924.

have been carbonized. The makers of these retorts say that segmental retorts are preferable, because owing to the smaller sections, greater uniformity during the manufacturing operations can be ensured.

Messrs. Koppers' have furnished some useful data relative to the use of their chamber ovens for town gas manufacture in the United States of America. Some of their ovens have been in continuous operation for fifteen years without any repairs, so that they say it is impossible to suggest what the probable life will be. The average flue temperature is 1,350°, and the net carbonizing period is 11 hours 5 minutes.

Mr. T. Glover allowed me to visit the Bishop's Bridge works at Norwich at a period when a house containing sixteen beds was down for overhaul. The settings are all of the Klonne generative type. Silica bricks are used in the combustion chambers and in the centre of the cross walls, and 83 per cent. siliceous bricks on the outside of the setting. The retorts cxamined were of the siliceous type, Serial No. B6. The works' officials stated that they had been worked for 1,853 days at an average temperature of 1,315°, the weight of charge being 14 cwts., which is carbonized in twelve hours, and that the total throughput per retort was 2,500 tons. I would suggest that, when the retorts have been refronted, they will last for a considerable period. The above results suggest that well-burned siliceous segmental retorts are eminently suitable where moderate temperatures are adopted.

Mr. S. N. Wellington has furnished data relating to the inclined chamber plants on the Continent and at Darwen. He states that the capacity of the chambers constructed of Stettin silica is 8 tons per charge; the working flue temperature ranges from 1,300° to 1,400°. At Hamburg, they approach 1,500° and the make is over 15,000 cubic feet per ton straight gas (cal. val. 510-520 B.Th.U. gross) with English coal. With regard to the Darwen plant, the chambers are built up of the Stettin fireclay material and have been in use for nine years. The installation has given exceptionally good results and the refractories are still in good condition. It is the considered opinion of Mr. Wellington that silica material is the only refractory which should be used in coke ovens and gas works, if progress is to be made.

It must be admitted that the manufacture of fireclay and siliceous retorts has not reached finality as regards improvement; possibly competition will stimulate the manufacturers of the latter type in the direction of improved texture and the development of a refractory, which, whilst not remaining rigid at the highest temperatures, will be more suitable than silica for the engineers who still prefer to carbonize at moderate temperatures.

Rigidity and Maintenance of Shape at High Temperatures.—Silica refractories will stand higher temperatures under conditions of load than fireclay goods. It is, therefore, a natural consequence

that silica retorts should replace the older types of siliceous or fireclay material. In spite of this, however, the illustrations which have been published recently, showing the condition of fireclay retort installations after an extended run at relatively high temperatures, suggest that the problem of choosing a suitable refractory material is not quite so simple as it appears at first sight. The following factors have a direct bearing upon the life of the material:—

1. Types of setting—with special reference to the nature of the cross walls and the proportion of retort covered by same.
2. Working temperatures, with indication of possible fluctuations.
3. Composition and physical properties of retorts.
4. Type of machine.
5. Cross-sectional design and size of retorts.
6. Proportion and type of ash present.
7. Throughput per unit.
8. Liability to form scurf.

Mr. Bromley, the engineer and manager of the works at which the exceptional working of fireclay retorts mentioned above has been obtained, kindly gave me permission to visit his plant. Having regard to the fact that these retorts are made of fireclay, it is interesting to know that they have operated for a working period of 2,660 days, carbonizing 20 cwt. charges in 12-hour periods, with a stoking machine of the Drake type in use, and with abnormally high working temperatures (for fireclay) of 1,370° to 1,420°. The latter figure has been subjected to independent verification by many persons. I have no other record of fireclay retorts giving such consistently good results, but possibly confirmatory evidence may be forthcoming from other plants (see Fig. 1).

This is a case of a refractory material which, judged by the usual standards, is exhibiting abnormally good qualities. Considering the matter from all sides, I came to the conclusion that the behaviour under load is a prime factor in the case. I have discussed the matter with Mr. A. J. Dale, B.Sc., and he puts forward what appears to be a very reasonable explanation. During some recent work on the softening of refractories under load Mr. Dale carried out two distinct sets of experiments:—

(1) Determination of the nature of the subsidence occurring under load before the temperature at which complete failure takes place is attained;
(2) Determination of the rate and amount of subsidence under load at a constant temperature of 1,350°.

As can be readily seen, the latter test provides some measure of the rigidity of refractories at temperatures well within practical working limits. His results, which will be communicated at a later date, suggest that certain classes of refractories remain fairly rigid under load at high temperatures, not far removed from those at which complete breakdown occurs. Other

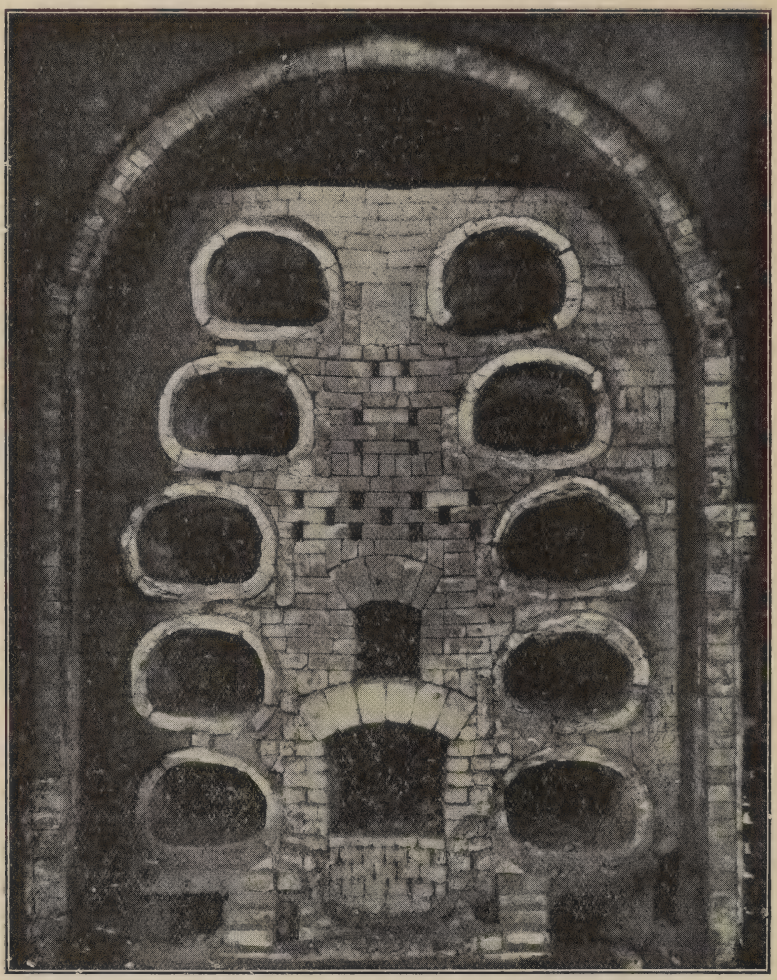


Fig. 1.—Moulded B4 Fireclay retorts after 2660 days (Drake's setting.) A3 silica in chamber and centre of cross walls; fireclay remainder.

types deform at relatively low temperatures. While silica belongs to the first class of materials, fireclays in general belong to the second, so that a possible explanation lies in the fact that this particular fireclay (and possibly others) are peculiar in maintaining a "silica" type of structure at elevated temperatures. An alternative explanation lies in the fact that the maintenance of porosity at elevated temperatures may allow the infiltration of carbon to proceed to such an extent that the retort may become a carbonized

clay substance, which possesses a higher refractory value than normal clays. This subject has already received attention by Bradshaw and Emery, and Lessing, and has formed the subject matter of a patent by J. Smith.

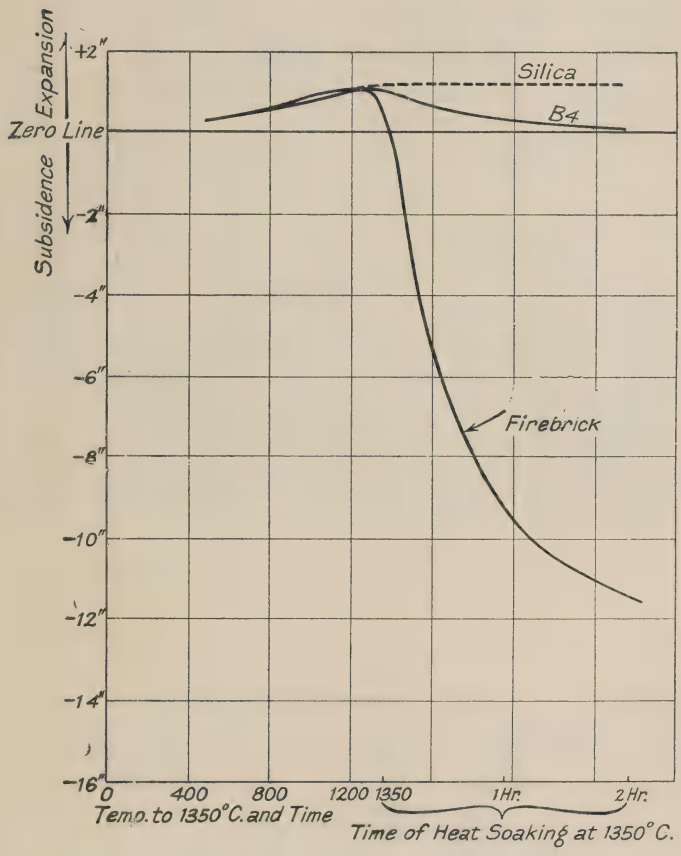


Fig. 2.

Showing comparative behaviour under load of 50 lb. per sq. in. at 1350° of well-fired silica, B4 material, and low-grade firebrick.

The following data relating to the working behaviour of some of the fireclay and siliceous retorts have been passed for publication by Mr. W. B. Leech (see Figs. 3 to 7,

Heavier Charges.—I have been unable to elicit much information which would lead me to believe that, other factors remaining

SUMMARY OF OBSERVATIONS MADE DURING A VISIT TO BECKTON WORKS.

House No.	Serial	Make	Temp. °C.	Working days	
2	B7	Segmental	1380	520	Very good condition.
	B4	Moulded			
3	B8	Segmental	1st yr. 1325 2nd yr. 1350 3rd yr. 1400	940	Setting was down, the retorts were examined from combustion chamber side, and apart from a covering of dark brown slaggy material they are in excellent condition.
5	B4	Moulded	1370	1530	Setting had been let down because the two top retorts had given way. whereas eight full sets of silica retorts in same house were in excellent condition.
6	A1	Segmental	1410-1420	280	"All silica settings." The behaviour of these two houses will probably decide future practice.
7	A1	Segmental	1410-1420	230	
8	A1	Segmental	1350-1350	530	Good condition.
	B6	Moulded	1350-1360	530	
	B7	Moulded	1350-1360	530	
12	A1	Segmental	1380-1390	180	Perfect condition.
	A2	,,	1380-1390	180	,,
	A7	,,	1380-1390	180	,,
	B6	Moulded	1380-1390	180	In one bed retorts pushed up as in Figs. 3-5 due to excessive expanion of cross walls.
	B8	Segmental	1380-1390	180	
12	A1	Segmental	1400	2150	No distortion—excellent shape. See Figs. 6-7.

constant, the introduction of silica retorts would enable heavier charges to be burned off in unit time. This is natural, inasmuch as the general practice during the last ten years has been to carbonize with full retorts, irrespective of their type. However, Mr. Chew has had a battery of silica retorts in use for 410 days, and he reports that: "The fuel used is 75 per cent. slack together with 25 per cent. screened and un-screened coal; the carbonizing period is 12 hours, but we are obtaining heavier charges with silica retorts."

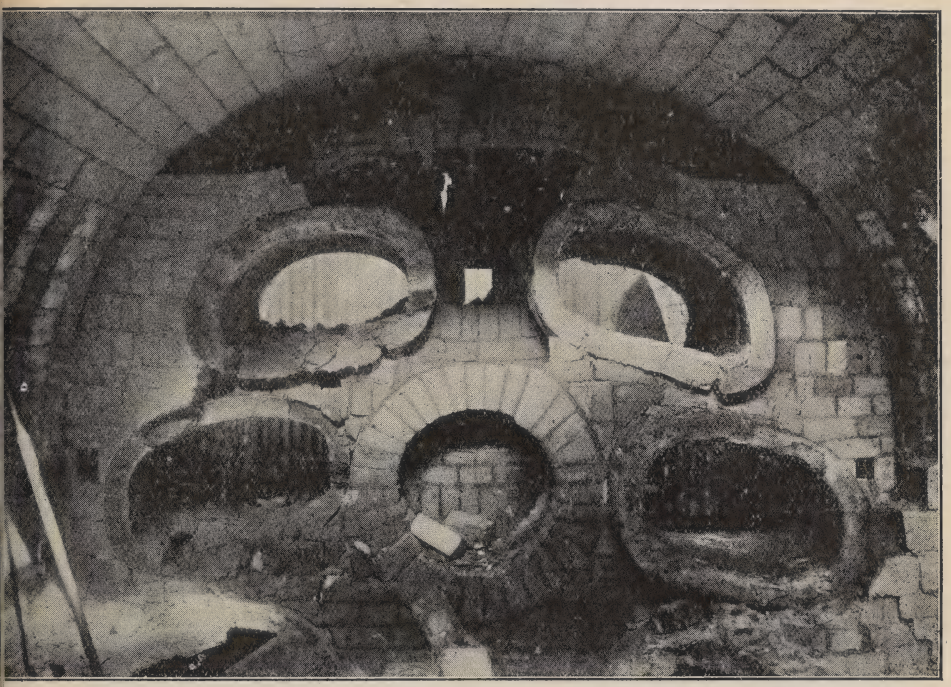


Fig. 3.—Beckton. Moulded fireclay retorts after 940 working days. A1 silica in combustion chamber; Stourbridge fireclay in remainder.

Abrasion.—The silica retorts which have been inspected have withstood scouring action very well. It is of interest to note that the silica retort manufacturers emphasize the fact that their goods are specially toughened, in order to resist abrasion. Well-fired fireclay and siliceous retorts are not lacking in this respect.

Mr. Morrison, whose experience with silica and siliceous goods extends over a period of twenty years, states that he has had under close observation composite retorts, in which the sides and arches were constructed of silica and the base of fireclay. In some cases the fireclay did not withstand the scraping effect of the rakes and pusher heads.

Scurfing.—There is no agreement between the users of silica retorts on the subject of the deposition of carbon and the removal thereof. In a general way, the removal is mainly effected by the cooling and burning effects of air currents. It would be of interest to ascertain the behaviour of silica in smaller works where "stop end" retorts are in use, since under these conditions more mechanical treatment is required to remove the scurf.

Fig. 4.—Beckton. Another bed after 940 working days.

Ash.—While at the Beckton works, I examined a setting which had been worked for 21 days and then shut down; one tier was built of silica, and the remaining tier of siliceous material. The differences, when seen from the combustion arches, were very marked. The silica retorts were substantially as set, whereas the siliceous ones were covered with a brown, semi-glazed mass, obviously due to the interaction of the ash and refractory. It should, however, be noted that this tendency to become covered with a semi-glazed mass soon after being put into use, is not necessarily a criterion of the quality of a refractory, for, in many cases, this coating forms such an impervious mass as to prevent further trouble.

Cracking.—It is admitted that, in general, moulded fireclay retorts exhibit a tendency to crack after a comparatively short life, as compared with segmental silica retorts. This fact, however, cannot be accepted as evidence that silica is more resistant

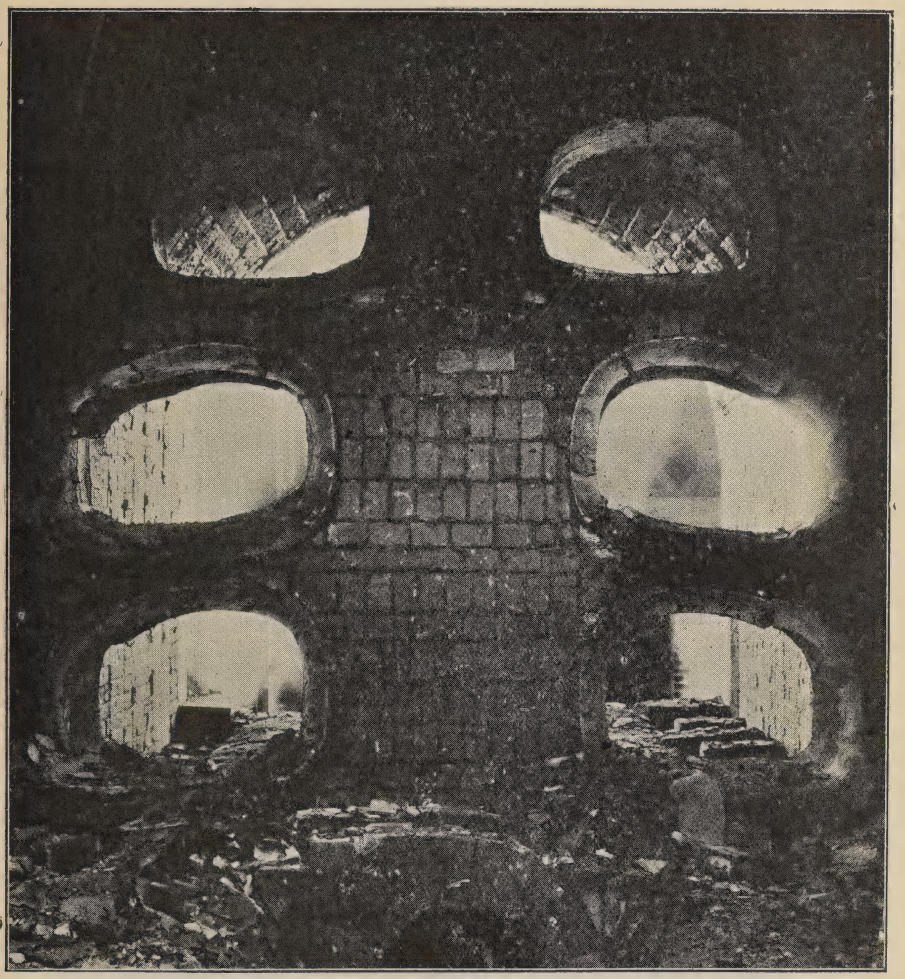


Fig. 5.—Beckton. Another bed after 1170 working days.

to cracking than fireclay.

In order to obtain a real criterion, segmental or moulded refractory material of each type should be compared (see Fig. 8).

Corrosion.—Mr. Foxwell, M.Sc., on behalf of Messrs. Koppers Ltd., has furnished me with the following interesting note relating to the effect of sodium chloride on refractories:—

"I have examined the action of salt on bricks and while, of course, most of my observations may not be given, I may say that I have found that silica, whether as quartz, cristob-

alite, or tridymite, is attacked by fused sodium chloride, with formation of sodium silicate, although this action is not very rapid. On the other hand, if clay is taken, the action of the salt is to form a compound containing about 28 per cent. of Na_2O, which cannot be washed out by water or acids. I do not know whether any explanation of the immunity of silica brick has yet been given, but although I have no experimental evidence to back up my suggestion, it has always

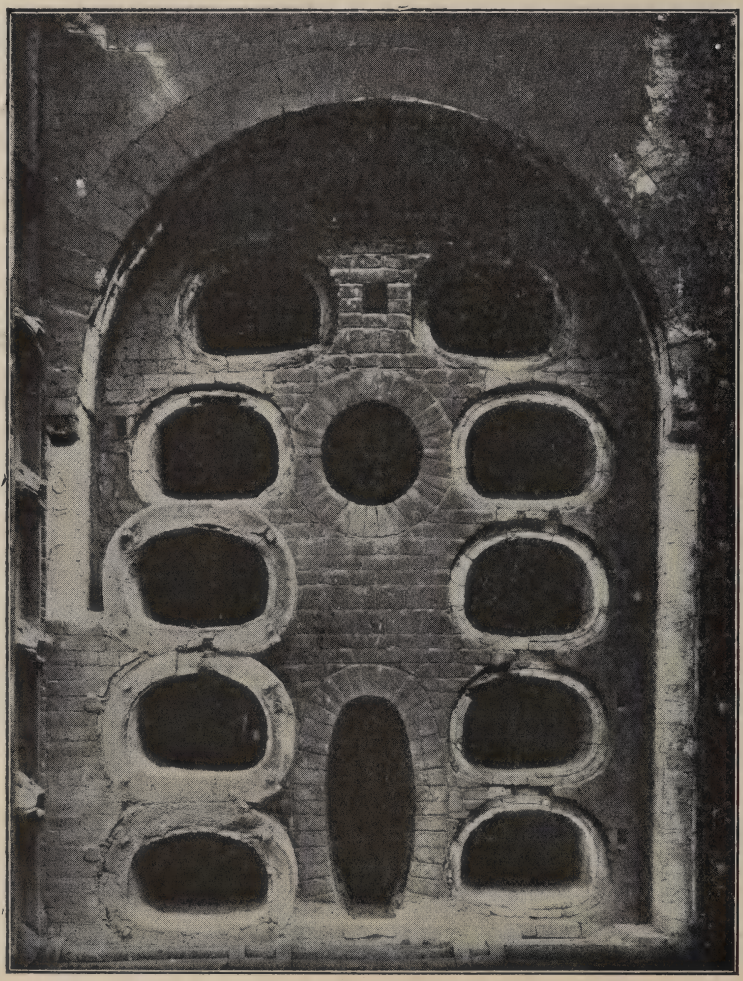


Fig. 6.—Segmental A1 silica retorts after 2150 working days. A1 silica in combustion chamber; Stourbridge in remainder.

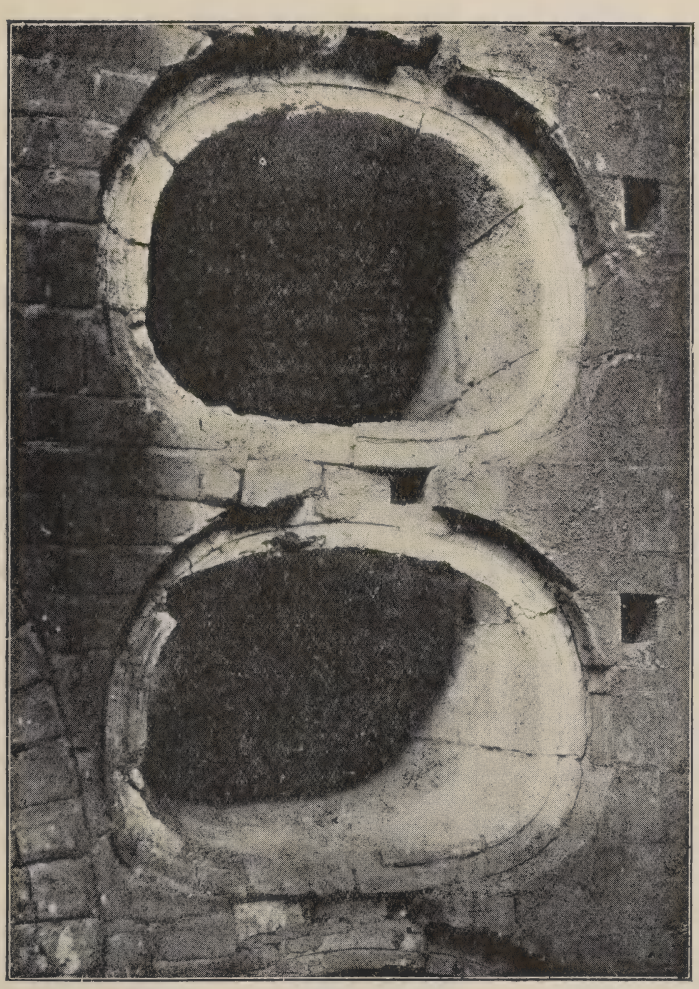
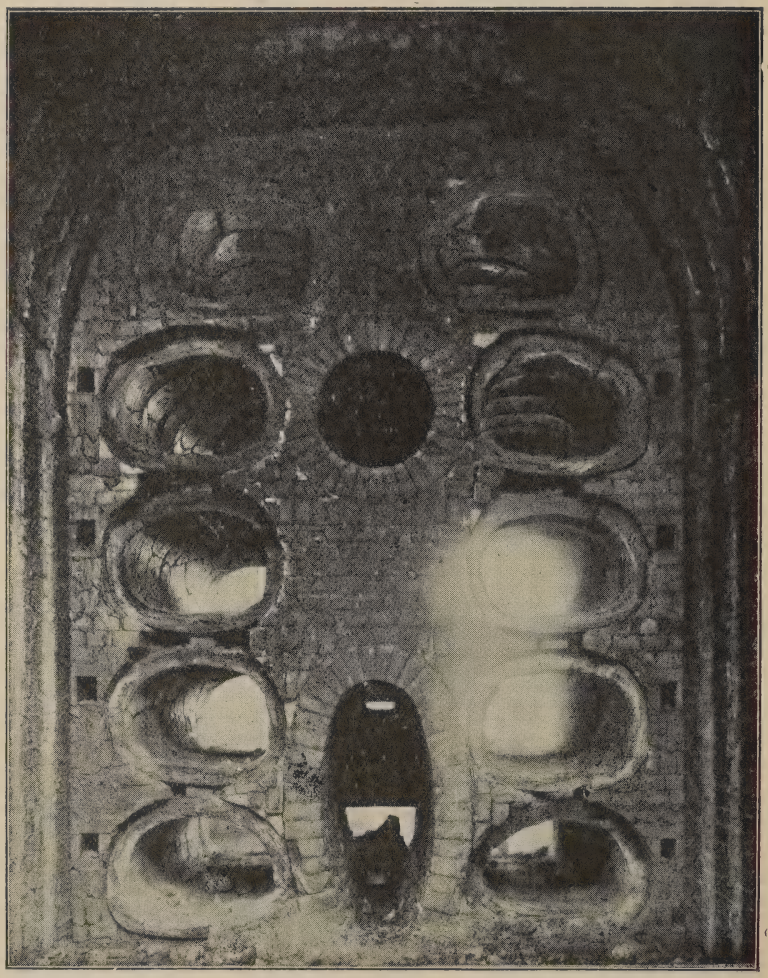


Fig. 7.—Enlarged view of second and third tiers in fig. 6.

seemed to me possible that the lime has a great deal to do with it. It may be that a lime-silica complex is formed which acts as a protective coating over each of the silica granules. There is some evidence for my view in that we have found in practice that a brick containing 91 per cent. of silica but with no lime, failed within less than a year, whereas a brick with 95 per cent. of silica and lime-bond has stood successfully for many years in the same ovens carbonizing the same coal."

Disadvantages.

Excessive Expansion, reversible (or temporary) and permanent.—The nature of the expansion data, which are supplied to the ccnstructional engineer by the physicist as physical constants of silioa material, deserve a close study. When refractory goods are heated in industrial furnaces, they undergo two distinct alterations in their linear dimensions. The first occurs at relatively low temperatures, and if the refractories are cooled to normal temperatures after this heating, they return to their original size—



Ffg. 8.—Beckton. Another bed after 2150 working days.

hence the term reversible or temporary expansion. In other words the property in question is the unavoidable thermal expansion common to most solids when heated. Secondly, when heated to higher temperatures, a series of changes occur, the nature of which varies with the chemical and mineralogical composition, texture, and previous heat treatment of the goods, either at the brick works or during service. These modifications are irreversible or permanent. In the case of a good silica rock, it can be said that the permanent linear alteration is always an expansion and is accompanied by a decrease in specific gravity. Similarly the normal variation in fireclay is a permanent contraction. When fireclays are hard burned there is a slight increase in the specific gravity.

Dr. Mellor[11] and other workers have carried out investigations on the volume changes occurring in firebricks with the "Coppée" apparatus, which involves the use of full sized 9-in. bricks. Other academic workers in many countries have reported values in close agreement with those given by the use of the Coppée dilatometer, but in these latter cases the tests have been on a laboratory scale only. For our purpose it will be convenient to summarise some of the results reported by Houldsworth and Cobb[12]. During the heating of a raw unburned fireclay there is a steady thermal expansion, until a temperature of approximately 540° is reached; the rate of expansion is accelerated between 570° and 600°; above 650° no further increase occurs. Well-defined permanent contractions occur at 880°, 950° and 1,080°, which is the upper limit of their experiments. They have examined the behaviour of a silica brick which had been fired previously to Cone 14. Starting

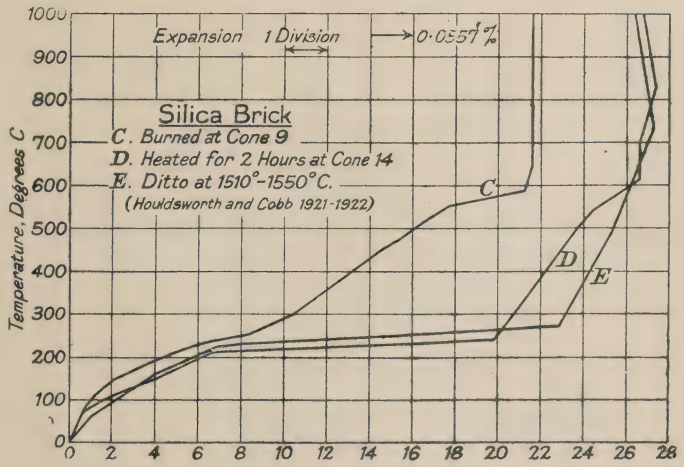


Fig. 9.

11 Mellor, Trans. **17**, 325, 1918.
12 Houldsworth and Cobb, Trans. **22**, 111, 1923; and **21**, 24, 1922.

from the cold state, it was found that the length increased regularly up to 200°; from 200 to 250° an extremely rapid expansion occurred amounting to 0·75 per cent. From 250° to 550° the sample expanded regularly, followed by a more rapid rate of expansion between 550° and 600°. All the low temperature changes are temporary and amount approximately to 1·5 per cent. Further irreversible and permanent volume increases were noted at the higher temperatures.

I am indebted to Messrs Woodall, Duckham, Ltd., for the following information:—

> "With regard to the expansion of silica settings as compared with fireclay, we find that a fireclay retort 26 ft. in length, has an expansion from cold to a working temperature of 1,290°, of about 2-in., while a retort of the same length constructed with a central zone comprising 14 ft. of silica expands approximately 3¼-in. up to 1,400°. After three months working at this temperature the total expansion from cold becomes approximately steady at 3½-in. Owing to the fact that, during the warming up stages, the total expansion is of a composite nature, *i.e.*, the temperature of the fireclay work above and below the silica and the temperature of the upper part of the silica zone being higher than the bottom, it is difficult to give any definite figures relating to the expansion of the silica at various temperatures. The above figures indicate a total expansion of the silica of approximately 1·4 per cent. for the 3½-in. rise (probably comprising 1·2 per cent. reversible and 0·2 per cent. permanent), and a further 0·1 per cent. permanent, making a total of 1·5 per cent. for the 3½-in. rise. From our observations, approximately 70-75 per cent. of the total expansion of silica settings takes place during the warming up stages and before any colour is visible in the combustion chamber."

The present writer, as a result of works experience, suggests that it is possible to produce firebricks which have zero volume changes when worked at moderately high temperatures. It should be recognised that, in this direction, the firebrick manufacturers have made rapid progress. It is impossible to lay down a definite percentage, type, or grain size of silica admixture to a fireclay, as being required to affect the purpose. However, once a standard has been decided upon, uniformity of grading, homogeneity and firing treatment require constant supervision, if satisfactory results are to be obtained.

The firing of the refractories is, undoubtedly, the factor which decides their behaviour in use, since this regulates the permanent volume changes. Probably everyone present has had experience with fireclay retorts which have lost their shape, even when worked at relatively low temperatures; in most cases this

defect would not have occurred had the heat work in the oven been greater than that imposed upon the retorts during use.

A number of substances such as lime, pyrites, etc., have a catalytic effect in speeding up the conversion of silica into tridymite. These materials, however, have the disadvantage that they lower the refractoriness, and as a result, they cannot be used in those cases, in which the goods are to be used under stringent conditions.

In the production of gas retorts, however, it is possible, and in my opinion, *advisable*, to make use of such admixtures in order to ensure more complete conversion with its accompanying reduction in permanent expansion. In some instances the silica retort manufacturers use one mixture only and that the one most suitable for the roof of steel smelting furnaces. However, it is interesting to know that other firms recognise that the gas industry demands specialised refractories and have made the necessary modification in order to produce goods likely to give the best results when used in towns gas works.

Many instances have been cited with respect to the ill-effects due to volume changes of silica cross walls. Mr. Leech has furnished pictures from which Figs. 3-5, have been prepared. At Beckton, I saw a similar defect in which the up-throw was about two inches, and this would probably increase as the high temperatures were maintained. The author is convinced that some of the alleged failures of moulded fireclay retorts have been due, not to the poor quality of the retort, but rather to the use of underburned silica bricks and blocks in the superstructure and cross walls.

Summarising, it can be said that, with all types of refractories, the reversible thermal expansion is unavoidable; but the manufacturerers have a modified control over the extent of the permanent expansion, and since it is the latter which is of vital importance to the user, it is the maker's responsibility to see that the point has proper attention.

It is obvious that the user must have some means of checking the quality of the goods he has received, and a test which will indicate whether the firing has been satisfactory is most desirable.

Consequently the standard after-expansion test has been adopted, and up to the present has probably been satisfactory. However, it may be that, as more laboratory and works data become available, other tests will be substituted. For silica refractories several alternative proposals have been made. These can be broadly divided into three groups:—

1. Methods involving the micro-examination of thin sections. (See appendix to present paper.)
2. Methods involving the determination of refractive indices. (Houldsworth & Cobb).
3. Methods involving the determination of specific gravity.

It has been shown that when a series of refractories has ap-

proximately the same percentage of silica and of lime, the true specific gravity is a direct measure of the firing treatment, and this, in conjunction with porosity, provides an indication of the probable expansion when put into use in industrial furnaces.

Fortunately, the composition of the available silica retort materials does not vary very much, hence determination of specific gravity is very useful. A specific gravity can be quickly and accurately determined without the use of elaborate apparatus, and I would suggest a more extended application of this method. Middleton has shown that silica bricks having a standard mixture and fired in industrial kilns to—

1,380° had a specific gravity of 2·43;
1,430° had a specific gravity of 2·35;
1,530° had a specific gravity of 2·23.

Restated, this means that, with an increase in the firing temperature of 150°, the decrease in permanent expansion was reduced by 1·3 per cent. Making allowance for the slight differences which may occur with other types of silica rocks, the above results may be taken as representative figures. The permanent expansion in practice is considerably greater than the theoretical, owing to the reorientation of the material.

This aspect of the behaviour of silica materials has been dealt with at length in order to make it clear that the most objectionable feature, from a constructional point of view, is amenable to improved manufacturing methods. In general, the improvement in quality is very marked; the manufacturers of silica refractories must not be content with anything but the best. In one case brought to my notice some silica segments were badly cracked; in fact, in order to complete a bed that was urgently required, the management were passing all goods with a maximum crack of 1 inch in length, relying, of course, on the support afforded by the cross walls to obviate danger.

At one works, I saw large batches of siliceous segments that were obviously underburned. It should be realised that the modern gas engineer is more conversant with the properties and behaviour of refractory materials than was the case some years ago, so that the manufacturer has to exercise a certain amount of discretion before he releases goods of inferior quality from his works.

The contractor is not only concerned with the expansion of the retorts and walls, but also with the increased stresses set up in the superstructure by the permanent expansion of the silica blocks at the higher temperatures. Messrs. Robert Dempster, Ltd. have taken out a patent which is of interest. The keystone of the producer arch is reinforced in such a manner as to provide a super-imposed or inverted abutment for support of the combustion arches.

Fig. 10 shows the lay-out of the arch and combustion

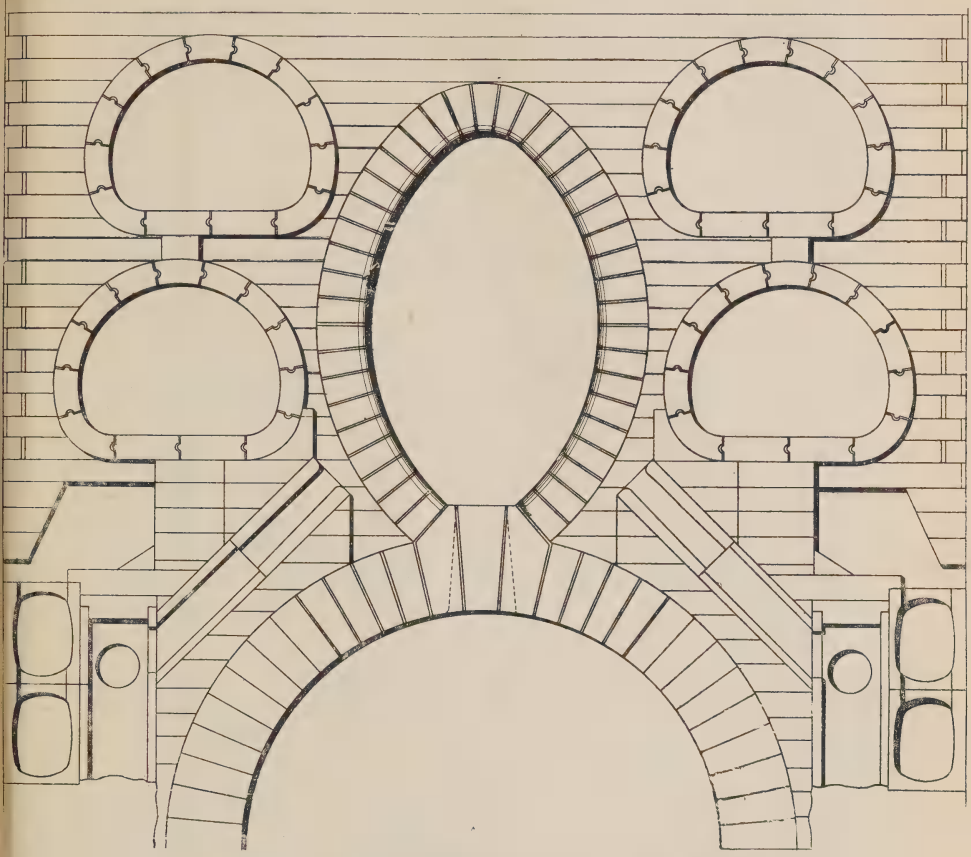


Fig. 10.—Dempster Keystone producer block.

chamber. It is obvious that, by the use of these blocks, the distance between the "legs" can be reduced; or, in other words, a more elliptical combustion arch can be built.

Special Precautions required during Setting.—Considerable trouble has been experienced in making allowance for the peculiar expansion which takes place in silica constructions on heating. This trouble is solely due to the fact that constructional engineers have not had, as yet, the same length of experience with silica materials as they have had with fireclay. As soon as the necessary experience in applying the physical laboratory data furnished in connection with the material has been attained, the trouble will entirely disappear. Meanwhile, among the experiments now being tried are the use of wooden packings, contractile clays, stays

fastened with lead washers, etc.

Messrs. Robert Dempster, Ltd. have taken out a patent in which they claim that, with the use of plastic siliceous clay (having an 8 per cent. drying contraction) in the joints, the thermal expansion taking place between 200° and 580° is gradually absorbed. Similarly, the joints between each segment resting in the stay walls should be made of siliceous clay and the walls built up tight with the retort.

I have inspected a number of settings where silica retorts are in operation, and was especially interested in the experimental settings at Beckton. At these works practically all the carbonizing contractors lay down settings of their own design, incorporating their own ideas for the counteracting of the temporary and permanent expansions. In addition, Mr. Leech and his staff have had a number of experimental settings built, and in one house alone eight distinct methods of packing have been tried. The information regarding the settings is carefully recorded and discussed at periodical staff meetings. Mr. Leech has kindly provided Fig. 11, which shows the methods now adopted in their all-silica settings. While at the above plant I inspected a setting built to this standard, which had been used for gas making for three weeks. Careful examination showed that the vertical joints were in substantially the same condition as when built; the wood packings had disappeared and the walls were under weight (Figs. 12-13).

Gill[13] has given an interesting summary of the practice adopted at the South Metropolitan Gas Company's works; and Harston[14], in his admirable paper, goes into greater detail as to the conditions at Norwich. But in both these cases siliceous and not silica retorts are in use.

It is essential that the temperature be increased very slowly during the heating-up stages, since the faster the "heats" are raised the greater the permanent expansion. It is interesting to note that the graph on page 379, shows clearly the actual temperatures at which the greatest care is necessary and also that, the harder the fire to which the silica goods have been subjected at the works, the lower the temperatures at which the maximum thermal expansion occurs.

It is my opinion that, if the silica refractories used in the settings conform to the present standard specification for after-expansion, then very little trouble need be expected in horizontal practice; if, however, the combustion chamber temperatures are raised, then a revision of the specification is necessary, since, as the temperature rises the tendency to expand increases beyond the limits of the specification.

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13 Gill, TRANS., **22**, 377, 1923.
14 Harston, *Gas J.*, **166**, 530, 1924.

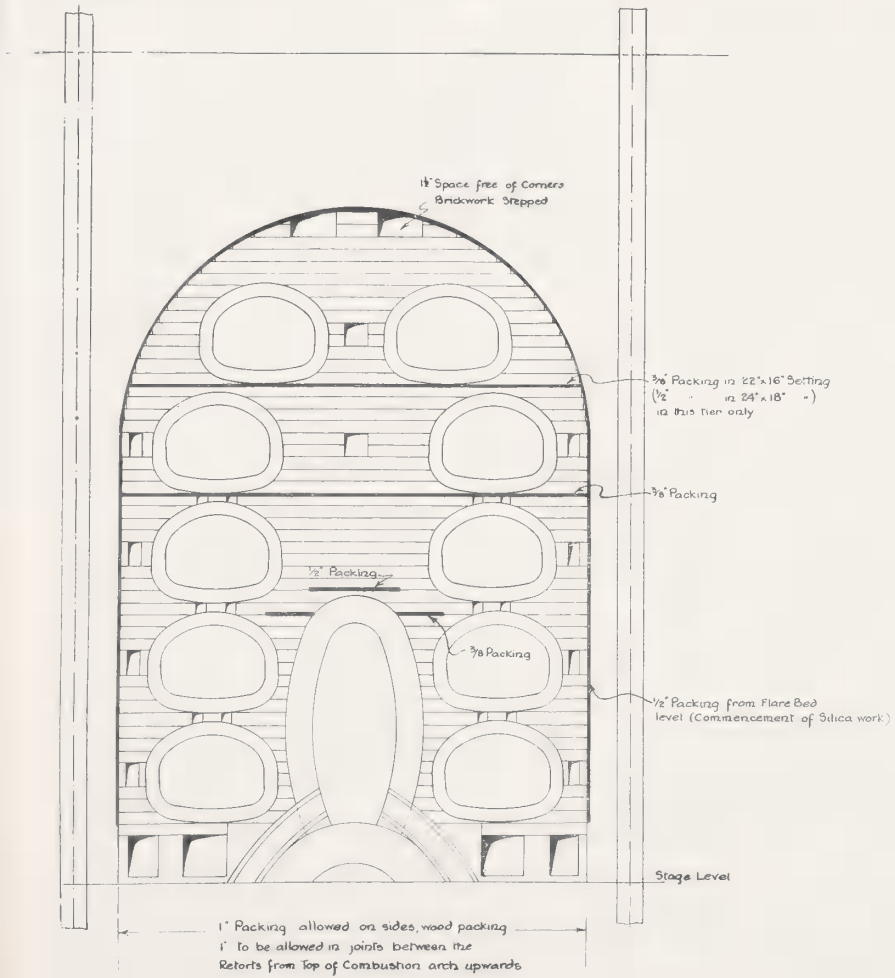


Fig. 11.—Beckton Standard Setting, showing allowances for expansion.

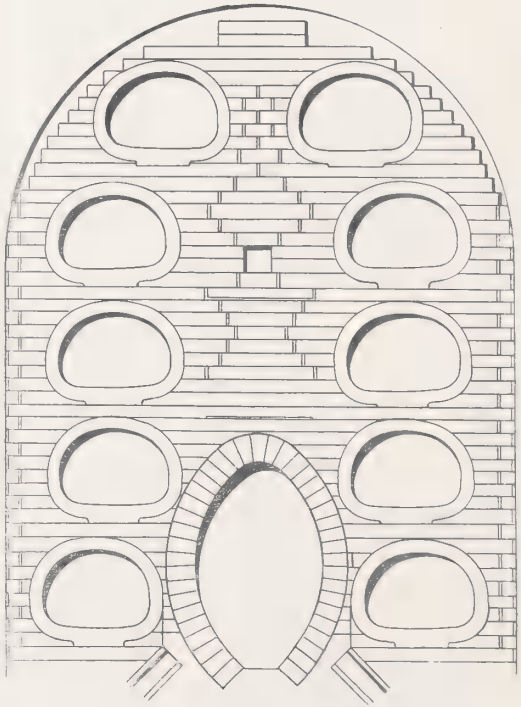
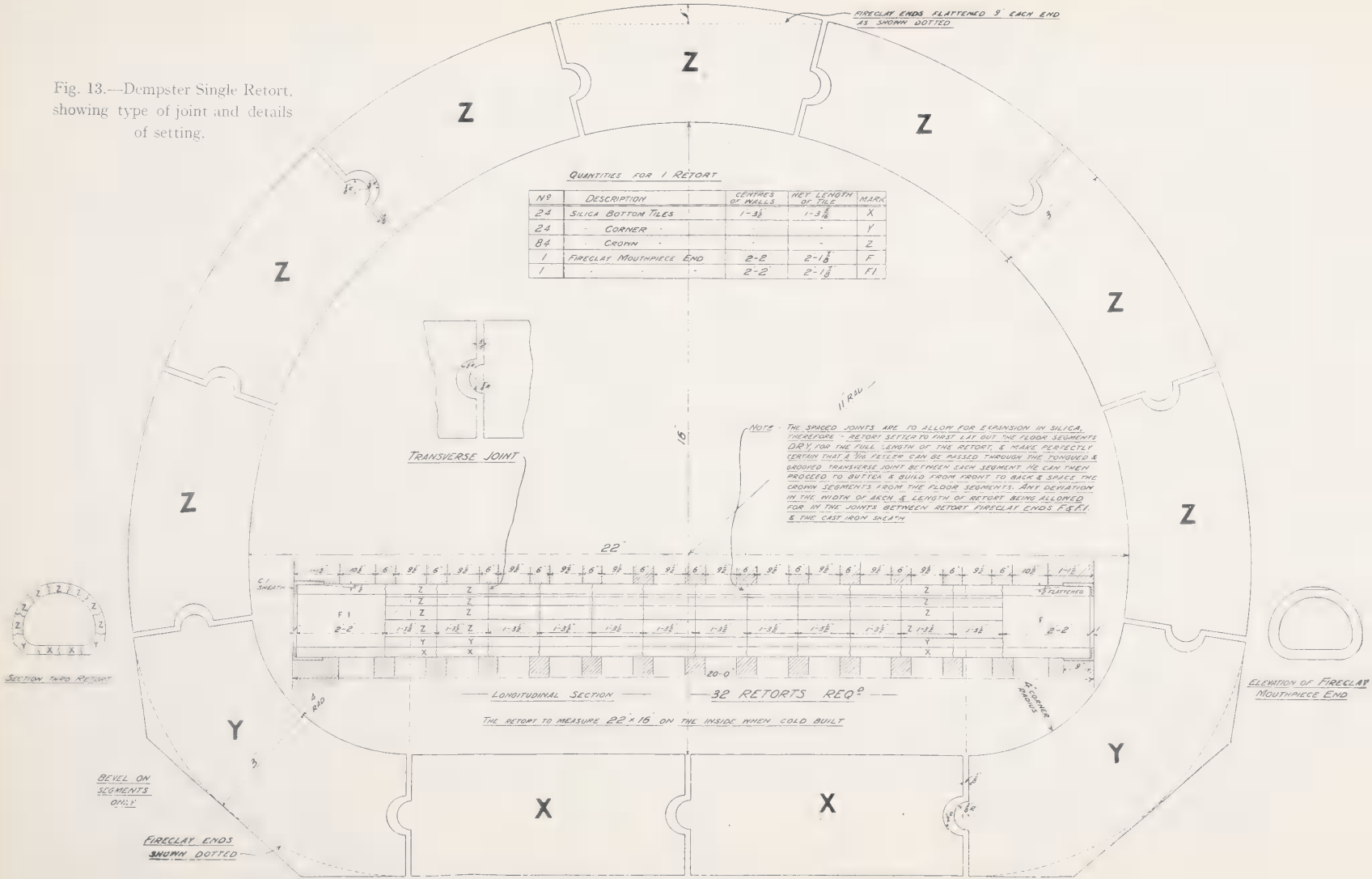


Fig. 12.—Dempster Standard Setting, showing allowances for expansion.

Fig. 13.—Dempster Single Retort, showing type of joint and details of setting.



Nº	DESCRIPTION	CENTRES OF WALLS	NET LENGTH OF TILE	MARK
24	SILICA BOTTOM TILES	1-3½	1-3 7/16	X
24	" CORNER "		"	Y
84	" CROWN "	"	"	Z
1	FIRECLAY MOUTHPIECE END	2-2	2-1 7/8	F
1	" " "	2-2	2-1 7/8	F1

Wear and tear effects due to alternation of temperature, e.g., spalling.—During the war period, considerable losses were experienced in the metallurgical industries through the spalling of silica bricks. It was proved, in the majority of cases, that the defect was primarily due to the fact that the demand was so far in excess of the supply that, to a certain extent, quality had to be sacrificed for quantity.

Comparing fireclay with silica, there is no doubt that the former is less liable to spall. I know of one silica retort setting, originally built of silica throughout, which, after a short run, had to be let down, so that fireclay mouth-pieces could be installed. In practice it is difficult (on account of spalling and cracking) when patching retorts to put into position silica segments, and in many cases siliceous segments are used.

Another interesting case was brought to my notice at the Beckton Works, where, within one setting, it was found that, when the retorts were scurfed, a layer of the retort was brought out along with the carbon.

An investigation by the interested parties showed that the porosity of those particular retorts was above the normal. I have enquired from several gas managers who are using silica retorts as to the occurrence of a similar trouble, but in no other case has the defect been observed. Further information was gained as the result of an inspection of silica retorts, which had been let down after a few weeks work. I noted that, midway along the setting and on the third tier, a piece of retort approximately 6 inches $\times$ 4 inches $\times$ $\frac{3}{4}$ inch was missing, and found the fragments in the base near the nostrils. On the opposite side of the chamber I was fortunate enough to locate a similar slab, held in position at one end by the cross-walls. This specimen is on the table for inspection. It is obvious from the ash residue, that the piece must have become detached at an early stage, probably during the heating up. In the same setting, several silica retorts were noticed which exhibited cooling cracks. It has been reported that, in certain silica coke-oven constructions in the U.S.A., the resident engineers were afraid to shut down. On the other hand, I have received a communication from a carbonizing engineer who has just returned from a visit to the U.S.A., to the effect that, after inspecting a number of coke-oven plants running for town gas, he failed to elicit confirmation of the report previously mentioned. Attention is drawn to the data on vertical retorts.

Determination when shut down.—While at the Keighley works, I examined a silica setting which had been let down. Mr. Bromley had the interior specially cleared, so that a thorough inspection could be made, and, apart from a small fracture at the junction between the fireclay mouth-piece and the silica, the retorts were in perfect condition.

I am informed that a silica battery at Liverpool has been shut down and re-started three times after the following working days:—

1st period	..	..	842	days.
2nd ,,	..	..	..	188 ,,
3rd ,,	..	..	..	164 ,,
4th ,,	..	..	..	178 ,,

The settings are still working and the condition is such that they will probably last a further two or three years.

Mr. Morrison reports that he has shut down his composite silica-fireclay retorts without experiencing any trouble. At the Beckton Works, where they have had an extended experience with silica retorts, the staff do not report any apparent deterioration when silica settings are shut down.

Lack of Mechanical Strength.—It is generally accepted that the silica refractory is more fragile than fireclay: but while it undoubtedly requires more care in handling, the modern product is quite capable of being transported and handled with ease.

Life under varying conditions not yet established.—I agree that exact data have not yet been published, especially as regards the behaviour of silica in comparatively small units.

It has been said that silica has been exploited only on large plants, where suitable apparatus and staff are available to ensure first class working conditions. Though this may be true, the larger units are carbonizing at higher temperatures than the smaller works. In any case, the margin of safety, so necessary where supervision is lacking, is much greater with silica than with siliceous or fireclay material. For instance, I have tested the temperature of a vertical installation which should have been working at a maximum of 1,320° and found it to be 1,450°. Fluctuations of this magnitude would be very injurious in normal fireclay settings.

Capital Outlay.—This aspect of the question is a very important one, but since the calculations involved are very simple and will vary within wide limits, it is not intended here to include a mass of data which may apply only in isolated instances.

VERTICAL RETORTS.

I have visited a number of plants, working under normal conditions and built by—

(*a*) West's Gas Improvement Co.,

(*b*) Woodall, Duckham Company,

(*c*) Drakes Ltd.

In order to obtain further information I inspected one installation of each type, which had been let down and cleaned. Mr. Harris, of Taunton, has furnished particulars relating to his

installation, which is a Leeds setting, built by Messrs. Goodall, Clayton & Co.

A.—Glover West.

The Leigh installation consisted of four Glover West bell-bottom retorts (new model). The upper and lower zones were constructed of fireclay bricks, and the central hot zone and combustion chambers of siliceous (88 per cent.) blocks. Two retorts were cooled and cleaned.

Condition of Refractories.—The fireclay firebricks in the "bell" portion were pitted and abraded; the harder fragments, though standing away from the face, could not be readily detached. The condition of the refractories as a result of the steaming is very similar to the structure of bricks, which have been subjected to the sand-blast test. The blocks in the siliceous zone were in very good condition, the surface being free from cracks. I noted that a fair number of the vertical joints were unsatisfactory. In one end of the retort, at a spot some 7 feet upwards from the mouthpiece joint, there was a small hole about ½-inch in width, the depth of one block. The fireclay refractories in the upper zones appeared to be quite satisfactory.

The second retort which the author examined was in substantially the same condition as the first as regards the general condition of the refractories, but there was no hole such as that occurring in No. 1 retort. A hole had been drilled in one of the blocks situated in the hottest zone in order to determine to what extent the bricks had been worn. It was found that the block was ½-inch thinner than when set into the retort.

Mr. F. Bowen, A.M.I.E.E., the manager at the Leigh Gas Works, has kindly passed the following data for publication:—

Fuel.—Lancashire seams, 4 feet, and Arley.
Commenced Gas-making.—January 10th, 1922.
Let Down.—March 10th, 1924.
Days Worked.—790.
Deductible for Scurfing.—Cleaning mains, furnace repairs, etc., 45 days.
Day's Gas-making.—745.
Tons Carbonised.—9,430.
Tons per Day per Retort.—12·65.
Steaming.—Pressure varied, 5 to 12 lbs. per sq. inch.
Mean Pressure.—8 lbs.
Super-heat.—None in general, but during specific test periods super-heated steam was used.

No serious deterioration of the refractories. A few small holes, arising from burnt-out joints, led to a slight loss of make near the end of period.

Average combustion chamber temperature in hot zone, 1,250°.

Practically no hanging of charges.

It is my opinion that this installation has done very good service, and I would suggest that the jointing material used is the only feature requiring attention. When the joints have been re-made the setting will have a further extended run.

B.—Woodall, Duckham.

Woodall, Duckham installation at Gas Street Works, Bolton, Battery of 7-ton retorts.

Refractories:—

The upper and lower zone, Scottish fireclay bricks.
The medial zone, A6 silica blocks (panelled).
Combustion chambers, A6 silica bricks.

Stated by the designer that their previous experiences led them to introduce new features to accommodate the expansion of the silica refractories.

Several retorts were cooled down and opened for inspection. Retort No. 22 critically examined.

Condition of Refractories.—The fireclay bricks at the top of the retorts were in good condition, with the exception of the four lower courses. The latter exhibited a peculiar crazed appearance, the network of cracks extending into the brick for about $\frac{1}{4}$-inch. The appearance of the upper 18 inches of the silica refractories was interesting, inasmuch as the surface was eroded in several positions, whereas between these patches the condition was very good. In this design of retort there are two bonding or supporting walls on either side, and the disintegration had taken place on the retort face in line with these walls. The depth of the patch was approximately $\frac{3}{8}$-inch, and starting at the top the width is approximately one foot, gradually decreasing in a tapering direction until at 18 inches the whole surface was sound. Downwards from this point the side walls were in excellent condition, the surface of the bricks was clean and free from cracks, whilst the joints were very firm. The appearance of the end walls in several isolated zones indicated that there had been a slight leakage of combustion gases into the retort through the cavities allowed for expansion. These cavities should theoretically have closed, but they did not do so owing to the total reversible and permanent after-expansion of the silica being less than was anticipated. The silica blocks were sound and the joints firm, in fact, the whole surface really formed a complete unit.

Erosion extended over a total length of 2 feet 6 inches in the vicinity of the steam nostrils, the surface being irregularly pitted across the whole section. It was not the extent of the erosion, but rather the peculiar manner in which it occurred, that was noted.

For example, one end of a block would be in good condition, whilst the remaining portion was completely eroded. In others the central portion was eroded and the two ends perfect. The

general tendency was for the finer parts to show up in vertical lines with the larger fragments of the refractory standing out in relief.

As distinct from above, the lowest portion of the retort and the large supporting blocks near the end walls were not in so good a condition. The surface was worn away to a fair depth, but the character of the partial disintegration was quite distinct from that previously noted about the steam inlets.

Discussion.—(1) Condition of silica bricks near the top of retort.

It is probable that the temperature of the retort face under normal working conditions is such, that any rapid fluctuation which may take place, due to varying moisture content or irregular working of the coal, would bring the silica within the critical temperature range in which considerable reversible expansion and contraction take place for a comparatively small rise and fall in temperature.

At the top of the retort the firebrick masonry is not eroded in the slightest degree; but it should be remembered that the first course in the silica zone coincides with the uppermost combustion chamber.

The fact that the erosion in the firebrick work was general around the steam nostrils, suggests that there is a close connection between steaming and erosion. The defective surfaces below are probably due to the abrasive action of the descending coke.

The following data were kindly supplied by Mr. W. J. Smith, gas engineer and manager:—

Fuel Used.—Lancashire coking coal.

Moisture Content.—3 to 5 per cent.

Retort in Use.—November 15th, 1921, to February 3rd, 1924, 5,500 tons fuel carbonized during 811 actual working days.

Steaming.—No direct measurements. Tests with waste heat boiler on an adjacent setting would indicate that about 450 lb. steam at 550° are admitted per ton of coal carbonized.

Hanging.—Trouble of hanging charges occurred at more or less frequent intervals; thought to depend on (1) quality of coal, (2) speed of throughput, (3) condition of retort (scurfing), (4) heats, (5) degree of steaming.

Scurfing.—Silica retorts appear to "grow" carbon more quickly and require scurfing more frequently than fireclay vertical retorts; carbon is just as easily burnt off.

Considering the throughput and the general methods of working, involving, as they do, combustion chamber temperatures in the silica zone ranging from 1,150° to 1,380°, the behaviour of the silica

refractories has been abnormally good; they will doubtless, with a few slight repairs, have a considerable life.

C.—Drakes, Ltd.

Mr. Cartledge, of the Congleton Gas works, kindly gave the author permission to visit his plant. It consists of twelve 3-ton retorts, of which, at the time of my visit,

5 were being used for gas making,
4 were "standing by" on low heat,
3 were shut down and cleaned out.

The installation has worked only during the last winter and the two retorts examined had been making gas for 40 days.

It may seem an unusual procedure to report on two plants after extended runs and then to discuss the condition of one which has been running for a few weeks only. However, my object on this occasion was to ascertain the effect which comparatively rapid cooling has in vertical silica constructions. "A6" silica blocks were used in the central portion of the setting and combustion arches, and Stourbridge fireclay bricks and blocks in the cooler zones at the top and bottom respectively. The silica refractories, apart from a few cracked blocks, were in excellent condition. I was very interested to find that, in the regions near the centre of the silica zones, there were a number of blocks, which undoubtedly exhibited cooling cracks, since the edges of the cracks were quite clean and free from the usual dark coloration present in older fractures.

Fireclay.—The fireclay refractories were showing signs of erosion, the appearance (not the extent) being similar to that described in the note on the Bolton plant. The appearance of one block was very unusual. During the firing in the oven a portion of the surface had been slagged, either from impurities in clay or from ash in the fuel. This denser portion was standing out in relief whilst the surrounding parts were eroded away. This suggests that texture and density play an important part in the resistance to erosion.

Mr. Cartledge stated that the temperature in the various zones of the setting ranged from 1,050°—1,380°. My own pyrometric readings confirmed this information. No figures were available as to the extent of the steaming.

Dessau Vertical Retort.

The installation at Taunton is an adaptation of the Dessau intermittent retort. Silica bricks "A3" were used in the chamber and cross walls. The retorts, which are 3 ft. 3 inches × 10 inches at the top, 4 ft. × 17 inches at the bottom and 14 ft. in length, are built of the same silica material.

Fuel carbonized.—Somerset smalls.
Weight of charge.—17 cwts.
Carbonizing period.—12 hours.
Worked for 370 days.
Present condition very good.

Mr. Harris states that the introduction of silica has enabled him to speed up the rate of carbonization considerably.

CHAMBER OVEN.

The following data concerning town-gas chamber-oven practice have been supplied by Messrs. Koppers. The information has been included, because it is quite likely that similar carbonizing methods may be tested out in Great Britain in large installations.

1.—*Oven Dimensions*:—"Height, 10 ft. 10 inches, length, 23 ft. 8½ inches, width 13½ inches. The dimensions for the largest ovens are:—Height, 12 ft. 6 inches, length, 20 ft. 8 inches, width 16 ft.. A narrow oven of slightly smaller capacity has the following dimensions:—Height 12 ft., length, 42 ft. 2½ inches, width 14 ft."

2.—*Moisture in Coal*:—"The coals used in the coke plants contain, on an average, from 3 to 5 per cent. moisture, but run as high as 12 per cent. when washed coal is used."

3.—*Chlorine in Coal*:—"As chlorine has no marked destructive action on silica bricks, the coals are not generally analysed for chlorine. The chlorine content, where it has been determined, is very low in American coals. In coals mined close to the seashore, in Nova Scotia, the chlorine content was found to be 0·05 per cent. This is high compared with the usual American coals."

4.—*Size of Coal*:—"At some plants the coal is crushed in a Bradford breaker, to 1¼ inches size, and then charged to the ovens. In other plants the 1¼ inches size is pulverised so that 80 per cent. passes through a ⅔-inch aperture. Pulverisation is always applied when different kinds of coal are being mixed."

5.—*English Tons per Charge*:—"The ovens mentioned in paragraph 1 have a capacity of 6·14 and 13·5 tons respectively (1 ton=2,240 lb.)."

6.—*Method of Charging*:—"No stamping is being used. The coal is always charged from a lurry car, through holes in the top of the oven chamber."

7.—*Free Space Above Charge in Oven*:—"Approximately 10 inches."

8.—*Distribution of Temperature on Flue Side—Top to Bottom*: —1,320° at top. 1,395° at bottom.

"This temperature is regulated to suit the particular kind of coal which is being carbonized."

9.—*Time of Carbonization*:—"A good average figure is 12 hours coking time for a 14-inch Becker owen. One of the installations

of 14-inch Becker ovens is running continually on 11 hour 5 minute net coking time with a flue temperature of 1,350°. We have no comparative figures with regard to coking time in fireclay or semi-silica ovens, as that type of construction has been entirely abandoned over here. Only silica ovens are now being constructed, and all ovens now being built in the States are of the Becker Type."

10.—*Corrosion*:—None.

11.—*Temperature of Charge at Conclusion of Carbonization*: 980°—1,040°.

12.—*Analysis of Gas*:—"The analysis of the gas varies greatly according to the kind of coal used. The following may be considered representative:

N_2	H_2	C_2	CO	CO_2	CH_4	C_2H_4	C_6H_6
6·0	47·3	0·3	6·8	2·2	33·9	2·4	1·1

Volume per cent.

13.—*Life of Oven*:—"Some of our plants have been in continuous operation for 15 years without any repairs to the brickwork, and are still running. We are, therefore, not in a position to tell the life of silica ovens. One plant has, to date, carbonized 100,000 tons per oven and is still in first class condition."

APPENDIX I.

Notes on Texture of Materials.

I. Silica Retorts.

*A*1. The ground mass of this refractory consists of spherical grains of uniform fineness, together with a few isolated fragments, having a diameter of approximately 7 mm., of a whiter material. The material is compact and moderately resistant to abrasion.

*A*2. This segment differs fundamentally from *A*1. The average grain size of the matrix is greater, and the particles are sub-angular. Angular fragments, 6 to 8 mm. in diameter, are scattered in fair proportion throughout the mass. The material is slightly tougher than *A*1.

*A*3. The matrix of this sample is of medium-sized grain, the largest particles not exceeding 5 mm. The grains are angular in form. The material is very tough and mechanically strong, and is, therefore, "transportable."

*A*6. The texture of this sample is such as to warrant close inspection. As in *A*3, the particles are sharply angular, but there are no large fragments. The surface of the piece is covered completely with a veneer, or skin, of a very hard material.

*A*7. The chief characteristic of this material, distinguishing it from all the other silica products, is the abundance of grains of medium size which it contains. The grading is well-proportioned, and the marked angularity of the larger particles is par-

ticularly striking. This segment also is encased in a skin of exceptional hardness. Both *A*6 and *A*7 are very hard and compact specimens.

II. Siliceous and Fireclay Retorts.

*B*1. This refractory contains grains chiefly of sub-angular, or spherical, form, together with a few relatively large spherical fragments. Though the cohesion between the matrix and the large particles is satisfactory, the material does not resist abrasion very well.

*B*2. This segment is hard and tough, and resists abrasion well. The proportion of grains between 2 and 4 mm. in diameter is high, though there are a few isolated fragments of approximately 6 mm. diameter.

*B*3. This appears to be a well-graded material. Thanks to good "packing" and cohesion, it will withstand rough treatment very well. The colour, though of no account in relation to serviceability, is exceptional.

*B*4. The otherwise highly satisfactory texture of this retort is marred by the presence of longitudinal laminations. The material, which is hard and tough, contains a large proportion of grains measuring between 3 and 5 mm. in diameter.

*B*5. The texture is fairly uniform and fine, the maximum diameter of the grains being 5 mm. The exceptional hardness and compactness of the material may be noted. However, a number of minute cracks can be seen to penetrate the surface to a depth of 1 to 2 mm.

*B*6*R*. This sample is of interest in that it consists, as can readily be seen, of a fireclay heavily reinforced with exceptionally large fragments of a siliceous nature. Despite the grain size, the cohesion between matrix and large particles is satisfactory.

*B*7. The charasteristic feature of this refractory is its vitreous skin, which is about 1 to 2 mm. in thickness, As was to be expected, the material, which is fine-grained and compact, withstood the abrasion test very well.

*B*8. The grading of this material is excellent. This fact, together with the uniformity of packing, explains the hardness and mechanical strength of the refractory. Cohesion between large grains and groundmass is remarkably good.

APPENDIX II.

Notes on the Micro-structure of Retorts described in the foregoing Paper.

By A. Scott, M.A., D.Sc.

Micro-structure of used and unused refractories:—Several of the materials described in this paper have been sectioned and brief notes on the micro-structure, both of the used and unused retorts, are given below:—

*A*2.—This material is composed of fragments of rock in a dark fine-grained matrix, which contains isolated crystals of quartz. Only the minute crystals have undergone conversion, all the coarser material still being in the low temperature form, except round the margins, where there is a peripheral development of cristobalite. The total amount of conversion is about 30-40 per cent., but the converted material is so finely ground as to make it impossible to ascertain its exact nature; much of it seems to be cristobalite. Some of the coarser rock fragments are highly converted and seem to be of the nature of prefired grog. Fig. 14.

*A*3.—This material consists of sharp fragments of a fine grained ganister-like rock in a matrix which has undergone a fairly high degree of conversion. The grain-size of the quartz crystals in the rock fragments is comparatively small, for partial conversion to cristobalite has occurred round the margins of each crystal where the proportion of quartz is low. This mineral forms a large proportion of the matrix. However, here and there areas occur composed apparently of a mineral with considerable double refraction and resembling the calcium silicate, wollastonite. The proportion of unconverted quartz is of the order of 35-40 per cent. Fig. 15.

*A*6.—In this material the rock fragments are much more altered than in either of the preceding cases and contain appreciable amounts of cristobalite. The matrix consists of a dark semi-opaque glass, containing an abundance of minute crystals of cristobalite, no tridymite being present in the section. The proportion of quartz in the material, as a whole, is of the order of 15-20 per cent. Fig. 16.

*A*7.—This material consists of angular fragments set in a doubly refracting matrix. The rock fragments show practically no trace of residual quartz but are entirely composed of cristobalite except round the margins where, occasionally, crystals of tridymite can be detected. The matrix contains a certain amount of clear material but is apparently mainly tridymite. The brick, as a whole, has undergone a high amount of conversion to the high temperature forms of silica and seems to have been very well fired. The amount of unchanged quartz in negligibly low. Fig. 17.

*B*3.—This material consists of minute subangular grains of quartz in a dark matrix in which it is difficult to distinguish anything. The quartz grains themselves have undergone a partial change around the margin, but the proportion of this mineral is still fairly high and approximates to 60 per cent. Fig. 18.

*B*12.—This is a piece of the siliceous material from the combustion chamber of a retort setting. Several very definite layers can be distinguished under the microscope. On the outside there is a black, apparently opaque layer about 1 mm. thick and containing comparatively few pore spaces. There is then a layer of black material with comparatively large pores, this layer being not quite so opaque as the margin and having a thickness of ap-

proximately 3 mm. Next, is a wider layer about 2-3 mm. in thickness, which appears to be a clear glass, except where it is in contact with the black along its margin. The white layer seems more opaque and contains numerous small white fragments. Beyond the white layer is a reddish layer which forms the main mass of the brick.

Under the microscope, the dense black area is seen to consist of a dark opaque glass, the opacity of which varies in different parts of the section. In this glass can be distinguished numerous cuboidal and octagonal fragments of a black opaque mineral which seems to be a spinel, the crystals of which are surrounded by an area of clear glass. It is probable that the opacity of the rest of the material is due to the presence of minute crystallites of spinel material.

The opacity of natural glasses is often similarly explained by the presence of innumerable minute crystallites in a clear glass. The porous area, under the microscope, consists of two types of material:—

(1) A similar glass which also contains elongated crystals which resemble sillimanite. Fig. 19.

(2) The other portion of this dark area is itself composed entirely of well shaped crystals of tridymite in a blackish matrix. It is of the same nature as the portion already described. The tridymite crystals are large and show the typical wedge and lath-shaped appearance. Black, spinel crystals, which seem to be mainly magnetic, occur throughout this area Fig. 20.

Occasionally, large fragments of clear material occur in the dark area and this seems to be composed partly of cristobalite and partly of tridymite. They seem to represent fragments of rock which have undergone conversion in the use of the material. The dark area gradually fades into the clear material already described as adjacent to it. (Fig. 21). The margin of this clear material is highly porous and consists of tridymite in a clear glass but the main mass of the white area seems to be composed of very minute crystals of tridymite containing local areas of cristobalite. The latter probably represents recently converted quartz grains. The amount of foreign material in this part of the brick is comparatively slight. Interspersed amongst the tridymite can be seen numerous minute crystals which are probably cristobalite. A partial analysis of this material has been made and the composition is as follows:—

SiO_2	88·64%
TiO_2	0·62
Al_2O_3	8·06
Fe_2O_3	0·68
CaO	0·76

From this composition it might be expected that the material consists of a form of silica together with a certain amount of sillimanite and this is what is actually found. The major portion of the brick consists of a fine ground aggregation of tridymite with numerous areas of cristobalite, the whole forming a fine-grained mass in which the original rock fragments can still be distinguished and into which occasionally foreign material seems to have penetrated. Microscopically, this part is sharply delineated from the clear area above mentioned. The cristobalite here undoubtedly represents converted fragments of rock, while numerous isolated grains, which have likewise recently undergone a change, can also be seen. No trace, however, of residual quartz is found even at a distance of more than 4 mm. from the black edge. Fig. 22.

A1R.—This material is a piece taken from the inside of a retort which had been in use for about 2,000 days. It is difficult to distinguish the original rock fragments and the sample now shows rounded crystals of quartz set in a dark matrix. The quartz crystals are surrounded by a layer of a material which seems to be composed of cristobalite and which undoubtedly represents the transformed margins of the original quartz. The matrix seems to be mainly cristobalite, although a number of minute crystals of tridymite can also be distinguished. An amount of black opaque material has penetrated the ground mass between the quartz grains but the latter are quite unaffected by it. The proportion of residual quartz is small and probably equal to about 8-12 per cent. Fig. 24.

A1C.—This is a piece of the same material taken from the combustion side of the retort, after having been in use for a similar period. In this case, the quartz has entirely disappeared and it is impossible even to delineate the original rock fragments. The material consists mainly of large, well-developed crystals of tridymite together with rounded grains with very low double refraction. Locally, in the isotropic ground mass, which seems to consist of glass, wedge-shaped twins of tridymite are frequent. The rounded grains with the low double refraction are apparently composed of minute crystals of cristobalite and represent quartz crystals which have undergone conversion during the use of the material in the setting. Similarly the coarse aggregates of tridymite throughout the piece are due to the transformation of the matrix from cristobalite to its present form. Fig. 23.

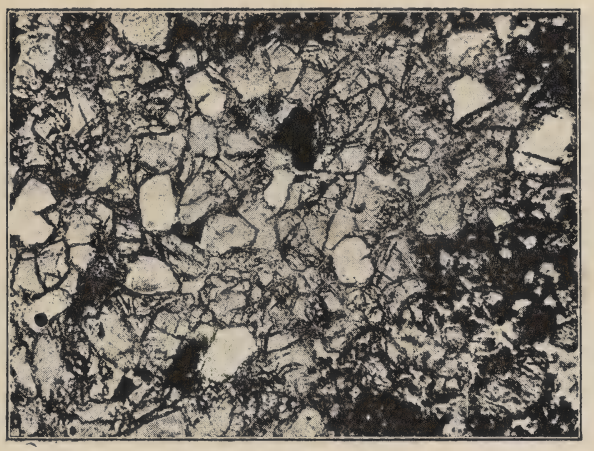


Fig. 14.

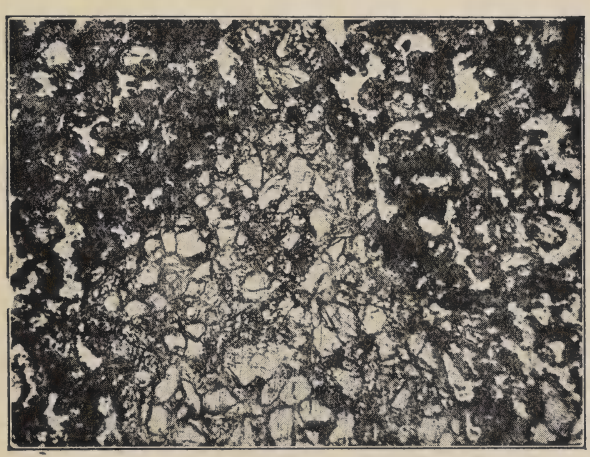


Fig. 15.

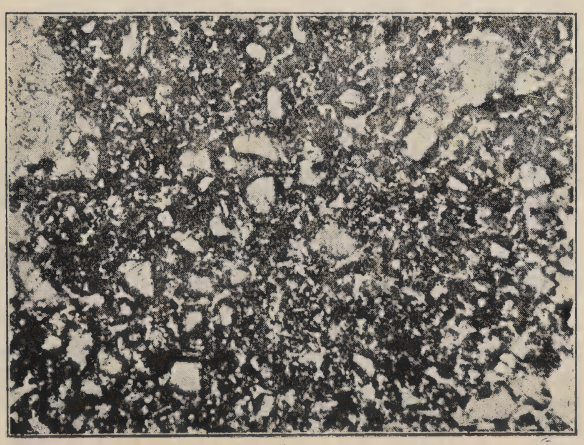


Fig. 16.

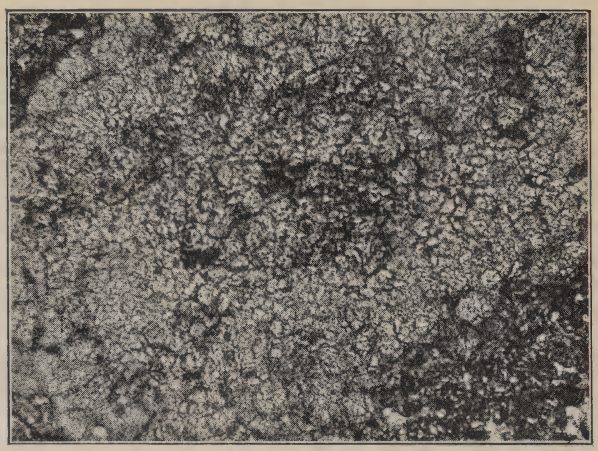


Fig. 17.

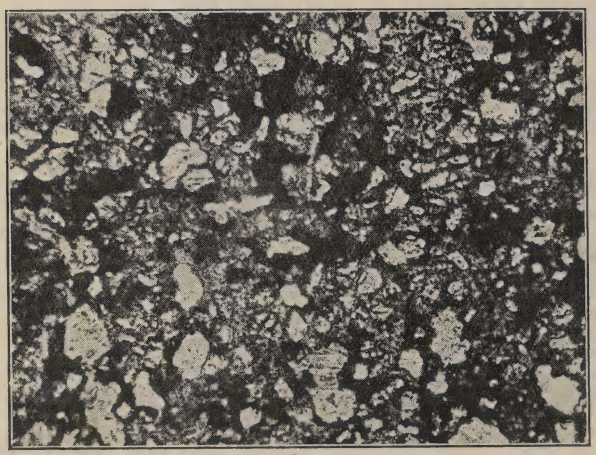


Fig. 18.

Fig. 19.

Fig. 20.

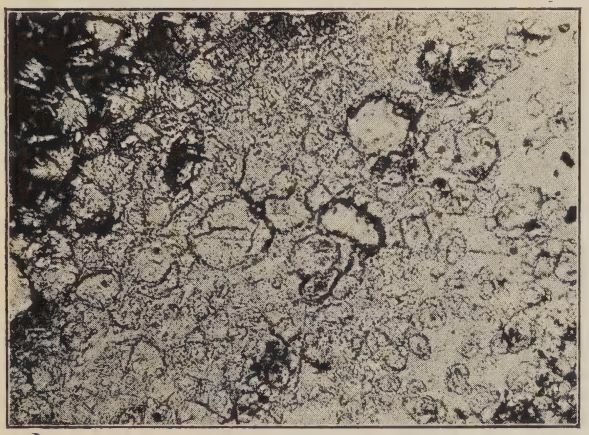


Fig. 21.

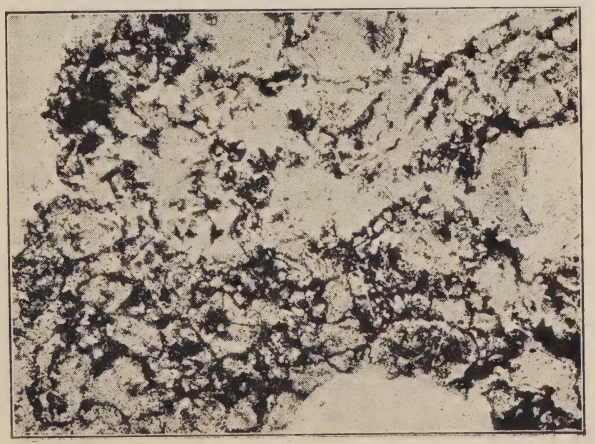
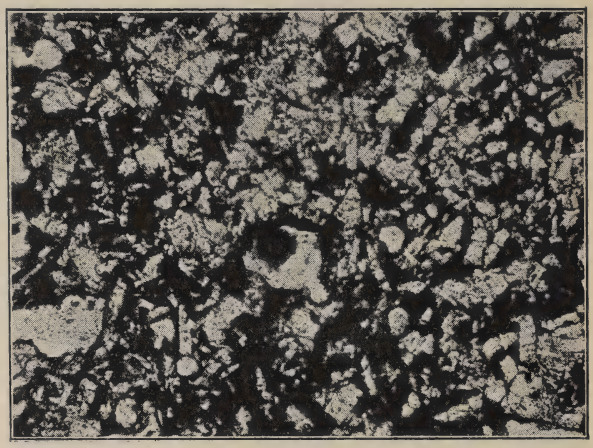


Fig. 22.

Fig. 23.



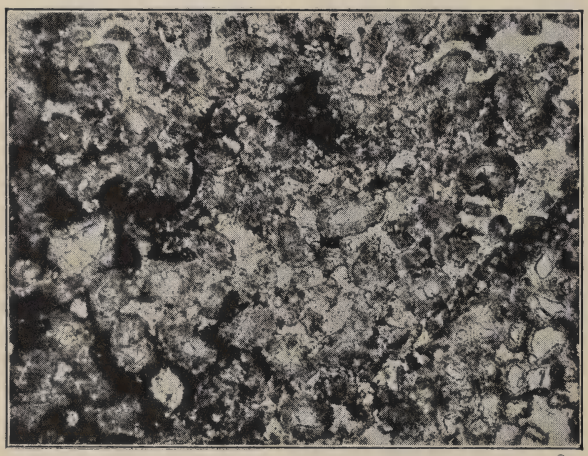


Fig. 24.

Description of Micro-Sections.

Fig. 14.—Micro-section of Retort A2 showing isolated quartz grains in a converted matrix.

Fig. 15.—Micro-section of A3 showing regular fragments containing quartz and set in a dark ground mass.

Fig. 16.—Micro-section of A6 showing higher degree of conversion than above figures.

Fig. 17.—Micro-section of A7. No trace of quartz can be distinguished, the mass of the material being cristobalite.

Fig. 18.—Micro-section of B3 showing clear quartz grains in a matrix which is partly opaque material and partly cristobalite.

Fig. 19.—Photograph of dark margins of B12 showing needles of sillimanite in the opaque glass together with tridymite in the light area.

Fig. 20.—Photograph of B12 showing numerous wedge shaped crystals of tridymite in the area next to the dark band.

Fig. 21.—Glassy area in Retort No. B12 mainly composed of minute cristobalite.

Fig. 22.—Main portion of used Retort B12 consisting of fine grained tridymite in a dark matrix which is diminished by foreign material.

Fig. 23.—Photograph of Retort A1C showing development of coarse tridymite in a material which is completely converted, no trace of quartz grains being visible.

Fig. 24.—A1R. Conversion in this case has been partial and a core of quartz can be detected in each grain, the margin of the grain being cristobalite.

XXXII.—The Constitutional Changes Occurring in Clays on Heating.

By

THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO.

(Work conducted by J. F. HYSLOP).

SUMMARY.

The facts established by the X-ray study of the constitutional changes in clay are:—

(*a*) Kaolinite completely breaks down at about 600°, forming a silicate which is stable to about 900°. This silicate is presumably $Al_2O_3 . 2SiO_2$. At the higher temperatures mullite is formed.

(*b*) *The X-ray patterns of natural sillimanite and of mullite, prepared by heating andalusite at 1,550° for 5 hours are different. The pattern of the mullite agrees with those obtained from fired clay materials. The mineral formed in clays at about 1,000° is mullite and not sillimanite.

(*c*) The formation of mullite occurs in all the clays examined by heating for 5 hours at 1,050°. The temperature at which complete stability is reached—that is, the point at which there exists only transformed quartz and mullite in the fired clay—varies according to the nature of the clay.

INTRODUCTION.

The data here presented resulted from an attempt to follow by X-ray methods the 500° and 900° changes in kaolinite, and to obtain information upon the stable compounds formed in fired clay. The method adopted was the examination of flat surfaces of the clays in order to obtain diffraction patterns which were used for identification, where possible, of the minerals formed on heating the clays for definite times at known temperatures.

PREPARATION AND HEAT TREATMENT OF CLAYS.

Small rods about 2 cms. long by 1 cm. diameter were made of china clay, siliceous German clay, plastic German clay, siliceous English clay, and of English ball clay. The rods were allowed to dry slowly, and were then subjected to 5 hour annealings at temperatures ranging from 450° to 1,450°, the temperature intervals being 100°. After this burning, the rods were broken in two, and the fractured surface was polished and then examined by the X-ray method.‡

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* Since the above was written, Navies and Davy (*J. Amer. Cer. Soc.*, **8**, 10, 1925) have given the detailed patterns for natural sillimanite and mullite.

‡ The preparation and examination of specimens were carried out by Mr. Rookesby and Mr. Gumm.

PREPARATION OF STANDARDS.

Since this work was not intended for crystal structure study, it was only necessary to obtain the X-ray patterns of known compounds for identification of the minerals present in the clays. Standard patterns were found for the following:—

(*a*) *Quartz*.—Very fine glassmaking sand was used.

(*b*) *Cristobalite*.—Prepared by heating fine sand in sodium tungstate flux at 1,550° for 5 hours.

(*c*) *Mullite*.—$3Al_2O_3 . 2SiO_2$—The white layer of a glass making pot, and (a sample of) a firebrick heated for 12 months at 1,500° were used for the standard mullite pattern. Mullite was also prepared by heating Californian andalusite at 1,550° for 5 hours.

The patterns of several other important minerals had naturally to be obtained. Among these compounds were tridymite, alumina, sillimanite, and kaolinite, but α quartz, cristobalite, and mullite were found sufficient for following the high temperature changes in the clays. This does not refer to the 500° change which will be discussed in a subsequent section.

SILLIMANITE AND MULLITE.

Since Bowen and Greig[1] published their work stating that mullite was the stable silicate at high temperatures, there has been some confusion regarding the nature of the silicate formed in clays on heating. The difficulties were emphasised by the fact that Shearer[2] found that the pattern of natural sillimanite agreed with that obtained by heating clays, and also by the work of Norton[3], who stated that natural sillimanite and synthetic mullite gave practically identical patterns.

In this work the pattern for sillimanite was obtained from a sample of the Indian mineral. This pattern did not correspond exactly with those obtained from the heat treated clays, or with those given by the white material obtained from used glass pots or from burnt firebricks. It also was not identical with the pattern of calcined Californian andalusite. The Californian mineral was heated for 5 hours at 1,550° and thereupon gave a pattern exactly similar to those of the burnt refractories. There is sufficient difference between the patterns of natural sillimanite and mullite to identify the compound in fired clay bodies.

CHINA CLAY.

The pattern of raw china clay was similar to that of kaolinite. After heating for 5 hours at 450° there was no marked change in the lines. These retained their original positions but showed decided changes in intensity. Heating for 5 hours at 550°, however, showed a noticeable change in constitution, a faint pattern just appearing, which became more definite at 650°.

This new pattern which appeared definitely at 650° persisted to 850°. The lines were diffuse, showing the presence of very small crystals, and were of low intensity, but the important point

is, that this new pattern is quite unlike that either of alumina or of any of the silica modifications. It must, therefore, be the pattern of a silicate which is presumably $Al_2O_3.2SiO_2$. An unsuccessful attempt was made to identify the lines of the new compound by calcining various hydrated silicates, but no patterns could be obtained from the resultant compounds. At 950° the lines of the new compound had entirely disappeared and were replaced by those of mullite. These were more intense at 1,050° and persisted at 1,450°. The silica formed by this reaction did not show in any of the X-ray films. It appears, then, that there is a stable silicate—presumably $Al_2O_3.2SiO_2$—existing between the endothermic and exothermic change points on heating kaolinite. The effect of heating may be briefly stated thus:—

	$Al_2O_3\ 2SiO_2\ 2H_2O$.
500-600°.	$xAl_2O_3\ y\ SiO_2$ ($Al_2O_3.2SiO_2$ probable).
900°.	$3Al_2O_3.2SiO_2+SiO_2$.

CLAYS.

A glance at the photographs given for the clay series will show that this is an excellent method for denoting the actual changes occurring in the constitution. The top pattern in each case is that of the raw clay and the temperatures increase on descending. In each clay the lines observed in the raw material were those of α quartz and kaolinite. In the case of the siliceous clays and of the plastic German clay, the α quartz lines were predominant. Those of kaolinite were the chief lines in the ball clay.

At the low temperature the disappearance of the kaolinite pattern was observed. The noticeable feature at the higher temperatures was the disappearance of the α quartz pattern, and

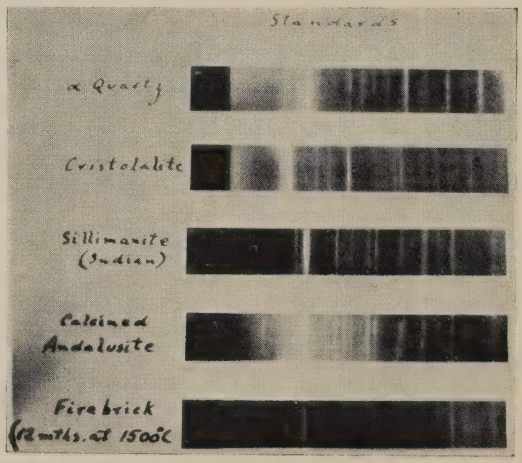

Fig. 1.

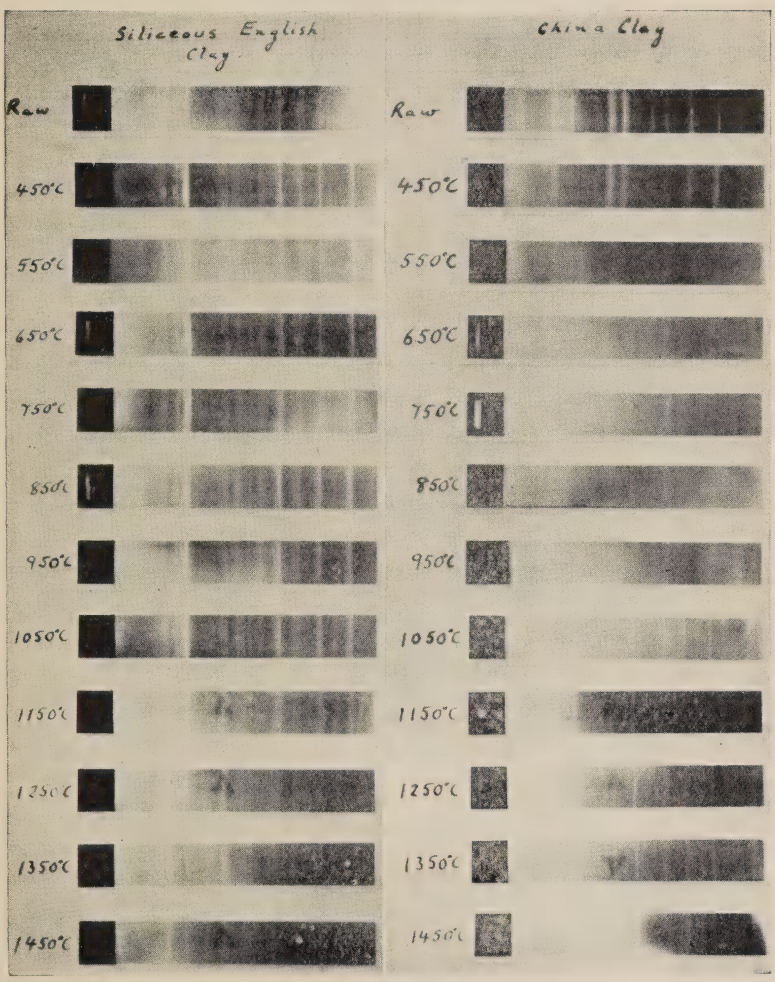

Fig. 2.

the appearance of a new pattern containing cristobalite and mullite lines. The quartz inversion occurred throughout a temperature range, whereas the mullite was observed at a definite temperature in all the clays, namely, 1,050°.

The importance of these patterns is that they show exactly when the clay has completely recrystallised giving stable constituents. The transformed quartz, in every case where identification was possible, was found to be cristobalite.

The following table briefly summarises the results.

Clay.	Principal Lines		Appearance of Mullite.
	α Quartz.	Cristobalite and Mullite.	
China clay ..	—	—	950°C.
Siliceous German..	950°	1050°	1050°C.
Plastic German ..	1150°	1250°	1050°C.
Siliceous English	1150°	1250°	1050°C.
English ball clay	950°	1050°	1050°C.

REFERENCES.

1. Bowen and Greig, *J. Amer. Cer. Soc.*, **7**, 238, 1924.
2. Shearer, TRANS., **23**, 4, 1924.
3. Norton, *J. Amer. Cer. Soc.*, **8**, 7, 1925.

XXXIII.—President's Address.

By A. G. Richardson.

THE past session has provided the Society with proof that further progress has been made in our pottery industry, and that the interest of our members has not abated. During the session we have had papers on a variety of subjects. Mr. Axel S. W. Odelberg again favoured us with a visit, and in a very explicit manner called attention to the value of the Dorr system of grinding pottery materials. Without doubt, this method of grinding has great merit, and suggests the possibility of obtaining a unit in size of particle which will be invaluable to the potter. The system should be worth a trial in this district. To me, it is a surprising thing that in this pottery district we seem to have no firms willing to try out a system of this character. The Pottery Manufacturers' Federation might find it to their advantage to try out such a method of grinding.

Mr. Harold J. Plant favoured us with a paper entitled "Pinholes, and Some Other Things". Though Mr. Plant's remarks were mainly confined to bone china manufacture, his method of dealing with the subject was so comprehensive that many of his data could be applied to other branches of the industry. In the second portion of his paper the speaker reviewed several important processes, including underglaze colours, and also the compounding and firing of glazes and enamel colours. One suggestion made by Mr. Plant was especially noteworthy, viz.: that whiteware glazes ought to contain three frits, (*a*) a lead frit, (*b*) a very soft borax frit, and (*c*) a very hard frit, the last mentioned to form the bulk of the glaze. Surely a modification of this character is worthy of close study under scientific observation.

During the session it was mentioned that an earthenware body was in use in the Potteries, which was free from crazing, peeling, or "spit-out." It would be of great value to the pottery industry if such a body could be put into general use, as, with less loss, goods could be sold at lower prices, and attract a wider market, which would increase employment. Such a production would also have the effect of raising the status of the industry.

Mr. Francis Lane's contribution on crushing and grinding was very interesting. Many data have been brought to our notice during the past few sessions relating to the fine grinding of pottery materials, but little information has become available relating to crushing and coarse grinding. Mr. Lane dealt with the fundamental principles of various types of machines, viz., jaw crushers, edge runners, crushing rolls, disc grinders, etc., and, like his earlier paper on pug mills, we shall be able to refer to his communication with confidence, knowing that he has a varied, practical experience along these lines.

There is no doubt that the meeting devoted to the "Question Box" was the most successful of the past session. Mr. Frank Worthington summarised his work in connection with the contraction of pottery cast from alkaline slip, and, though his conclusions were at variance with the usually-accepted practice, Dr. Mellor's explanation of the apparent abnormality showed that Mr. Worthington had opened up a new field for research in this particular direction. Mr. Walter Emery gave a contribution dealing with the flashing or devitrification of ware cast with soda slip. The views he expressed were somewhat different from those usually held, the suggestion offered being that the defect was a mechanical one. In support of this view samples were exhibited cast from a non-alkaline slip, showing the characteristic defect. It was stated, however, that the presence of alkalis probably accentuates the trouble. Mr. Ash in his maiden effort before the Society, dealt with the causes of milkiness in light blue printed ware. It was interesting to hear one of the contributors to the discussion admit that he had made use, with considerable effect, of information given at one of our earlier meetings. Dr. Mellor jocularly remarked that the treasurer might be credited with a percentage of the savings effected thereby. Freedom from crazing is the first essential in general earthenware, and Mr. C. D. Grimwade gave a very useful summary of various factory methods made use of in order to determine whether a batch of ware is likely to give good service. He suggested that a standard method be adopted, which would be acceptable not only to manufacturers, but also to foreign buyers, particularly in the U.S.A.

I wonder if any manufacturer of dinnerware has always escaped an epidemic of whirler plates ? If so, he has been saved much worry and anxiety, because the origin of this defect is elusive and most difficult to locate. But Mr. Gleaves' note on this subject certainly covered the possible causes, and during the ensuing discussion many people put forward their views. Mr. Lindley's statement, "Given right moulds, right profile, and correct setting of the profile, it is impossible to produce whirlers," caused many of the members some heart-burning.

Mr. S. R. Hind, B.Sc., gave an excellent report of a visit to the Osmosis plant at Carlsbad. There was much of interest in Mr. Hind's report, but there are still some points which need clearing up, and probably at some later date we shall be favoured with further information Later in the session Mr. Hind gave a very clear description of a new method of fritting by means of a rotary frit kiln, the heat being supplied by oil or gas. This kiln is now used largely in the U.S.A., and it is claimed to be far more efficient and economical than the frit kiln in general use in England. There seems to be great merit in this method of fritting, and some comparative costs were given, but it seems advisable that further information should be gained and some definite data brought

forward before any decision is arrived at concerning its claim to economy. During an interesting private talk between several members after this meeting, attention was called to the fact that two local members have developed a patent method of fritting, which claims to be more economical and much more efficient than this rotary frit kiln. Probably we may hear more of this during the next session.

A most important lecture was given during the session by Dr. Middleton (H.M. Medical Inspector of Factories), entitled: "Dust Counting." There has been much good work done in the Pottery industry to eliminate the "Dust evil," but I do not remember a lecture dealing with the subject having been given in a more lucid manner than that given by Dr. Middleton, and I am glad to know that further work is being carried out along similar lines.

An interesting evening was spent listening to Mr. Walter Emery's note on "Whieldon Ware," and examining samples of ware which had been found on the site of the old Whieldon Pottery at Fenton. Some excellent pieces of the potter's art were on view, of such merit as to call forth praise from many members present. The suggestion was made after this meeting that a committee should be formed of the younger members of the Society to investigate the various sites in the Potteries district where it is probable that pottery of real interest may be found. It would seem best that a volunteer corps of investigators should carry out such a work and report their findings to the Ceramic Society. To find ware, in good condition and of a high quality, which was made by the old potters, is always stimulating and full of interest to the new potters, and it makes us feel that we have yet much to learn.

Mr. Clifton Reynolds brought to our notice a patent tile-dipping machine. I know that tile manufacturers consider that their particular branch of the industry does not receive sufficient attention by the various speakers at out meetings. Consequently, the tile-dipping machine described and exhibited by Mr. Reynolds was specially welcomed by our tile-manufacturing members. There seems to be no doubt that, when several minor alterations have been made, the apparatus described by Mr. Reynolds will be capable of doing excellent service in the majolica tile trade.

At this point, I would like to ask the question, "Why not more papers from pottery students ? " With the facilities provided, and Dr. Mellor's encouragement, present-day students should realise what wonderful opportunities they have of serving a great industry by their efforts in research work, and of adding their contributions to the great work which has already been done by others. The need for research in pottery production is greater to-day than ever. The difficulties of pottery manufacturers appear to become greater instead of less, or is it that a higher general standard is demanded and economic conditions are compelling greater efficiency and less loss ? There are also new fields

to enter and new adventures into the unknown, in every phase of ceramics. The variations in pottery materials render the efficient manufacture of pottery a difficult proposition. The raw materials are particularly troublesome, *e.g.*, ball clay, china clay, flint, stone, felspar, fireclay, saggar clay, etc. And, seeing that the potter has no means to hand at the moment of standardising the properties of each of these materials, there is plenty of scope for scientific investigation concerning the classification of the various effects developed by the varying compositions and the varying physical properties of these and other materials.

In the general processes of manufacture there does not seem to have arisen anything of special note, but there are still many difficulties to overcome in the use of alkaline slips, which appear to be on the increase rather than diminishing, though it would seem, in many cases, that a better article would be produced by the jolley at a comparative price. In the use of alkaline casting slips there is still some trouble with pin-holes, and problems still require to be solved in connection with varying fluidities, variations in the time of casting up, etc. The numerous causes of such troubles have still to be made clear and defined. It would also be an advantage to investigate the best uses which can be made of scraps of waste clay in the production of this type of casting slip, and the best treatment to adopt to obtain a slip which does not possess the detrimental properties before mentioned. Research might also be undertaken into the possibility of making casting slip from raw materials, particularly as difficulties might arise as to the refining of the various materials.

There has been much progress made in drying processes. It is of vital importance to the potter that his ware and saggars should not only be thoroughly dried, but slowly and steadily dried, if he is to obtain the best possible results. The development of drying stoves has already provided a much more healthy set of conditions for the worker, and continued development along these lines seems to be of vital importance.

There is also the vexed question of saggar production. It is important that we should know the best method of making and the most suitable materials to employ, and in what proportions, to meet the needs of various types of pottery and the various conditions of pottery manufacturers. There is an enormous scope for scientific investigation in this field, in spite of the fact that so much work has already been done. The fact remains that, in the case of saggars, the manufacturers' losses are considerably higher than they should be, and this is one of the economic troubles of the present-day manufacturing potter. It is necessary to keep in mind also that, even with the best possible saggar mixture and mixing, there still remains the need for careful handling by the placers and drawers of ovens. I feel that much good would ensue if the marl-owners co-operated with the scientific aid that is

available in the Potteries, so that the best possible results could be obtained from their marls and clays, as it is obviously to their advantage that the potters should have the best and most suitable marls for their particular purposes. Good results to the potters would bring increasing prosperity to the district as a whole. I do not know that the cost of the marl-getting would necessarily be increased, or the cost of preparing the saggar marl be any greater, but if the product justified an extra cost for materials or their preparation, the ultimate gain would be undeniable. All will agree that more scientific methods are needed in respect of the winning of suitable saggar clays and their preparation. I would like to make a suggestion that, in connection with all saggar marls, a fair trial should be given to the dry method of mixing the saggar clay and grog to obtain a more perfect admixture than is possible by using the moist or wet marl, or even mixing by the layer process. I would suggest: (*a*) an intimate mixture of dry ground marl with dry drog, which mixture after being thoroughly incorporated, should be spread in layers and moistened with sufficient water to produce eventually a mass of sufficiently plastic marl as to be ready for use when pugged; (*b*) a similar mixing using wet grog instead of dry grog to mix intimately with the dry ground marl. In both cases, the marl mixture in its moist condition should be allowed to age to obtain a more perfect water distribution and to mellow the mixture.

There has been a great advance made in regard to the scientific methods of firing, *e.g.*, continuous biscuit and glost ovens and enamel kilns, as well as in connection with the firing of fireclay goods. Yet, seeing that there is so great a number of the old-fashioned ovens and kilns still in use, which, on the ground of expense or lack of room or other reasons, it would be difficult to replace, except in the course of many years, there is here, again, great scope for scientific research, in order that we may get the best possible results, both in regard to efficiency and economy. We must all admit that, in this particular section of our industry, owing to lack of definite, scientific methods, great loss is involved and a lower efficiency realised than ought to be the case. In addition, we have the smoke nuisance, so strongly complained of by those who are not engaged in our industry, but who, whilst one is prepared to agree that they are, no doubt, moved by the best motives, would be more patient if they were potters and had potters' troubles and trials to contend with.

There is also great room for investigation as to the most suitable fuels for the various processes of pottery manufacture. So long as the old-fashioned types of kilns and ovens are in use, so long will it be necessary to consider what are the best types of fuel for the various stages of pottery firing. Until it is found possible to fire the old-fashioned types of ovens and kilns with either

gas or oil fuel, under more scientific control, there will always be room for research here.

In reference to continuous ovens, there is a field for investigation in regard to a type which would be suitable for small factories. Another phase of the firing problem is the importance of oven and kiln atmospheres—the question of the effects, good or ill, promoted by different atmospheres—and the possibility of putting the atmospheres of ovens and kilns under real control.

There has been much discussion, extending over many years, concerning pottery glazes, and particularly in relation to the use of leadless and low-solubility glazes, as opposed to the glazes containing raw lead, with the view of ascertaining whether the admittedly high quality glazes which contain raw lead can be effectually replaced by leadless or low-solubility glazes, which seems very desirable from the standpoint of the health of the workers. There is still a difference of opinion on the matter, some people claiming that our lead glazes can be displaced, whilst others contest that claim. The fact remains that, for certain types of pottery, no glaze is equal to the raw lead glaze, and the rich effects rendered possible by the use of such glazes cannot be obtained either by leadless glazes or glazes of low solubility. So long as this is so, there is no reason why constant efforts should not be made to produce leadless or low-solubility glazes which can equal in merit the former raw-lead glazes. Meanwhile, let every precaution be taken to protect the health of the workers who are engaged in the glaze departments wherever raw-lead glazes are used.

Our old enemy, "Spit Out," is still with us. Whether it is present because we do not follow the advice freely given to us by the late Mr. Wm. Jackson, Dr. Mellor, Mr. Bernard Moore, and others, I cannot say; but is is still in evidence, and we shall all be glad to be favoured with a cure-all. However, in confirmation of the suggestion that slow biscuit firing, with an oxidising atmosphere, and the constant steady baiting of enamel kilns with plenty of air, will overcome the trouble, I can say, from personal experience, that "spit out" has been reduced to a very low level as compared with the high percentage of loss when the biscuit ovens were fired more quickly and with less air, and enamel kilns were fired similarly.

The extended use of lustres has brought in a new series of troubles which require investigation. How to produce lustres in bulk which are not liable to rub off; how to keep a constant brilliancy; how to avoid an iridescent surface when a plain surface is required; and how to avoid the cracked surface which develops on lustres—these are some of the problems which have to be solved in connection with lustres. Again, the extended use of self-coloured decorations in utility ware has rendered it necessary that such colours shall resist fruit acids. This opens up a field

for investigation as regards reliable bases for enamel colours to be employed for this purpose. Enamel kilns and enamel kiln colours generally afford a wide field of work which will probably occupy many years. If there could be evolved a series of simple, scientific data, which could be easily imparted to those who are engaged in the various departments of the factory, this would be of great advantage. If it were possible for, say, the heads of departments—particularly the mill, the sliphouse, the firing processes, and the decorating managers—to have special studies, which they could readily understand and assimilate, their efficiency would be considerably increased, and, with a head manager who is well trained in scientific, technical, and practical potting, our productions should reach a very high level. I do not think this an altogether too Utopian idea, but, rather, one to which pottery manufacturers should give earnest consideration, and confer with Dr. Mellor as to its possibilities. At present, unfortunately, any manager with a scientific training finds his special efforts more or less annulled owing to the difficulty in obtaining reception and co-operation in new and progressive ideas, or in the introduction of scientific methods, and much good work is lost owing to the lack of interest on the part of the workers, or through the clinging to methods and processes which have been in use for many years, but which could well be improved.

I am not suggesting that all things need alteration, but only that many things could be improved if the scientific mind of the worker could be stimulated. Much good work is lost through the mechanical attidude of the workers towards their particular duties. There are many reasons for this, but, from a scientific point of view, there is no reason why the worker's interest should not be specially aroused through the interest which is present in every phase of the potter's art. Probably a knowledge as to why certain things are done in the many processes involved would remove the mechanical effort and attitude of mind from the worker, to his advantage and in the interests of pottery generally. The productions of pottery have reached a generally higher level. The public have demanded a better class of general pottery; which is all to the good, as the worker finds more pleasure in producing a beautiful article than an ugly one. We, therefore, need the scientific and technical side of our pottery manufacture to reach the highest possible level. There has been great progress made, but we desire to climb still higher, and the Ceramic Society has still greater possibilities to achieve than it has already achieved.

A suggestion has been made that, as a means of developing active interest in connection with the Ceramic Society's meetings, a night should be set apart and called the "Students' Night," on which occasion pottery students shall give the papers, and only students be present, except, as a suggestion, the President, or a Vice-President, and the secretary of the Society,

so that there would be no restraint, and every encouragement would be given to free discussion. This would give an opportunity to those who are naturally hesitant of speaking in public to develop confidence. If such meetings provided free expression of opinion, then, in later years, the students, as active members of the Ceramic Society, would more readily enter into the discussions, and this would lead up to a freer interchange of views on the various subjects that come before the Society for consideration.

I think you will agree that the discussions on the papers which are read are not always exciting. Not that there is an absence of interest, but the fact remains that there is not sufficient interchange of ideas. This may be due to many reasons. More discussion might be induced if it were possible for a rough draft of the papers about to be given to be circulated to local members a few days before each meeting. I would suggest that it may be made possible for members to send in written statements expressing their views on the various papers, and, if they desire to do so, without revealing their identity. Also that readers of the TRANSACTIONS who cannot attend our monthly meetings be invited to do likewise. This may possibly tend to evolve a good deal of useful data, and increase the interest and sphere of usefulness of the Ceramic Society. We must not consider, even though we may have less discussion at our meetings than would seem helpful, that no real good results. It is not so; for, at times, it transpires that ideas suggested by the lecturer, or to which expression is given during the discussion, have developed into useful application later in the various spheres of pottery production. I trust that, during the coming session, all members of our Society will increase their interest in its proceedings and development, and that our pottery students will give us a great lead, justifying their heritage and the privileges and facilities which they enjoy under the inspiration and guidance of Dr. Mellor.

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TRANSACTIONS

OF

THE CERAMIC SOCIETY

VOL. XXIV.—1924-25.

ABSTRACTS.

Stoke-on-Trent:
Webberley Ltd., Percy Street Printing Works, Hanley,
1925.

INTRODUCTION.

THE following are abstracts from papers bearing upon the clay, refractories, and glass industries in the more important foreign journals as well as those of our own country. The abstracts are arranged roughly in eight main classes. The groups are constantly overlapping, and, to avoid repetition, a copious index is appended. This will enable any reference to be quickly found. Most of the journals quoted are permanently filed so that the full papers may usually be consulted by members of the Society. Full translations of any of the foreign papers can be obtained at a small charge. As a rule the abstractor indicates the "subject title" of those articles which, in his opinion, contain either no original matter, or matter not suitable for abstraction. These abstracts were made possible by a grant from the Joint Committee of Allied Pottery Manufacturers, and were compiled by Mr. F. SALT (with the exception of a few initialled).

The following particulars respecting patents may be of use to members:—

Country	Address	Cost
Britain ..	Patent Office, London	One Shilling (extra postage outside United Kingdom)
United States	Patent Office, Washington ..	Five cents
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Of Canadian Patents, manuscript copies only are obtainable. They may be secured from Fetherstonhaugh & Smart, or the Commissioner of Patents, Ottawa. Estimates of cost may be obtained in advance.

In ordering a copy of a patent, the number of the patent and year of the patent, the name of the patentee and the subject of the invention should be stated.

Titles of Journals Abstracted, with Abbreviations.

Allg. Tonind. Ztg... "Allgemeine Tonindustrie Zeitung" (Czecho-Slovakia)
Amer. Min..... "American Mineralogist" (American)
Analyst..... "The Analyst" (British)
Ber. D. K. Ges. .. "Berichte der Deutschen Keramischen Gesellschaft" (German)
Brennstoff..... "Brennstoff-Chemie" (German)
Brick..... "Brick & Clay Record" (American)
Brick Pot. Tr. J..... "Brick & Pottery Trades Journal" (British)
Brit. Claywr..... "British Clayworker" (British)
Bull. Imp. Inst..... "Bulletin of the Imperial Institute" (British)
Can. Chem. Met..... "Canadian Chemistry & Metallurgy" (British)

Cer..... "La Céramique" (French)
Cer. Ind..... "Ceramic Industry" (American)
Ceramist..... "The Ceramist" (American)
Cer. Vet..... "La Ceramica ed il Vetro" (Italian)
Cer. et Verr..... "La Céramique et la Verrerie" (French)
Chem. Age..... "Chemical Age" (British)
Chem. Met. Eng... "Chemical & Metallurgical Engineering" (American)
Chem. News..... "Chemical News" (British)
Chem. Tr. J. "Chemical Trade Journal & Chemical Engineer" (British)
Chim. Ind..... "Chimie et Industrie" (French)
China Rev..... "China Clay Trade Review" (British)
Claywr..... "Clayworker" (American)
Corr. Cer..... "Corriere dei Ceramisti" (Italian)
Deut. Töp. Zieg. Ztg. "Deutsche Töpfer und Ziegler-Zeitung" (German)
Diamant..... "Diamant und Glas-Industrie Zeitung" (German)
Econ. Geol..... "Economic Geology" (British)
Faenza..... "Faenza" (Italian)
Fenerfest..... "Fenerfest" (German)
Feuerung..... "Feuerungstechnik" (German)
Gas J..... "The Gas Journal" (British)
Gas World..... "Gas World" (British)
Gazz. Chim. Ital..... "Gazzetta Chimica Italiana" (Italian)
Giorn. Chim..... "Giornale di Chimica industriale ed applicata(Italian)
Glashütte..... "Glashütte" (German)
Glass..... "Glass" (British)
Glass Ind..... "The Glass Industry" (American)
Ind. Chim..... "L'Industrie Chimique" (French)
J. Amer. Cer. Soc. "Journal of the American Ceramic Society" (American)
J. Amer. Chem. Soc. "Journal of the American Chemical Society" (American)
J. Chem. Soc..... "Journal of the Chemical Society" (British)
J. Ind. Eng. Chem. "Journal of Industrial & Engineering Chemistry" (Amer.)
J. Soc. Chem. Ind. "Journal of the Society of Chemical Industry" (British)
J. Soc. Glass Tech. "Journal of the Society of Glass Technology" (British)
Kalk Schm.-Ztg..... "Kalk-, Gips-und Schamotte-Zeitung" (German)
Keramos..... "Keramos" (German)
Ker. Rund..... "Keramische Rundschau" (German)
Ker. Steklo..... "Keramika i Steklo" (Russian)
Met. Erz..... "Metall und Erz" (German)
Min. Met..... "Mining and Metallurgy" (American)
Nature..... "Nature" (British)
Pat. J..... "The Illustrated Official Journal (Patents)" (British)
Porz. Glas..... "Die Porzellan und Glashandlung" (German)
Pot. Gaz..... "Pottery Gazette" (British)
Pot. Glass Rec..... "Pottery and Glass Record" (American)
Prod. Chim..... "La Revue des Produits Chimiques" (French)
Quarry.... "The Quarry & Surveyors' & Contractors' Journal (British)
Rev. Mat. Constr. Trav. Pub. "Revue des Matériaux de Construction et de Travaux Publics" .....(French)
Sprech..... "Sprechsaal" (German)
Südd. Tonind. ..... "Süddeutsche Tonindustrie" (German)
Tonind. Ztg..... "Tonindustrie Zeitung" (German)
Tonwar. Ofen Ztg..... "Tonwaren Ofen-und Töpfer-Zeitung" (German)
TRANS..... "Transactions of the Ceramic Society" (British)
Trans. Faraday Soc..... "Transactions of the Faraday Society" (British)
Verre..... "Le Verre" (Belgian)
Zprávy Ceskoslov. Keram. Spol. "Transactions of the Czechoslovakian Ceramic Society".....(Czecho-Slovakia)

*** The first number represents the number of the volume, the last the year of publication, and intermediate numbers the page or pages where the subject is discussed.

Abstracts.

I.—RAW MATERIALS.

GENERAL.

ANTIMONY AND ITS COMPOUNDS IN CERAMICS.—L. Maugé (*Pot. Gaz.*, **50,** 171, 1925). The physical and chemical properties of antimony are briefly described. Antimony occurs naturally as the sulphide (antimonite or stibine), the largest beds being found in China. The method of extraction is outlined. Antimony oxide is used as a substitute for tin oxide in the pottery industry. Gold and vermilion antimony sulphides are prepared by adding the necessary quantity of sulphur to the ore (Sb_2S_3) to produce Sb_2S_4 or Sb_2S_5. Lead antimonate (Naples, or antimony yellow) is melted with lead silicate to form vitrifiable colours.

KAOLIN FROM FURTEI IN SARDINIA.—E. Repossi (*Rev. Mat. Constr. Trav. Pub.*, No. 184, 18B, 1925). Translation from the Italian *Rassegna Mineraria*. The geological formation of the deposits is discussed at some length. The kaolin contains practically no alkalis, lime or magnesia, not more than 1·85% of iron, 57-68% silica and 30-43% alumina (in the calcined product).

RAW MATERIALS: OCCURRENCE, PREPARATION, ETC.

"CELLITE" PRODUCTS FROM A MARINE DEPOSIT.—(*Chem. Tr. J.*, **76,** 132, 1925). A deposit of hydrated amorphous silica, estimated to contain thirty-three million tons, is situated ten miles from the Pacific coast in California. This deposit is formed of the minute skeletons of marine diatoms, the cells being hollow and, in many cases, intricate in shape. The accumulated mass has a structure and a porosity which render it of great value as a heat insulator. The so-called "cellite" products include various grades of light, bulky powder, and of quarried and moulded bricks. For heat insulation the powders are used alone or combined ; one coarsely-ground calcined grade serves as lining for furnace doors, being rammed into place after being mixed with a little Portland cement and water. Bricks cut from the beds have a crushing strength of 28 tons. Their thermal conductivity is less than one-tenth of that of ordinary firebricks.

SPECIAL SANDS.—W. M. Weigel (*Ceramist*, **5,** 177, 1924). A comprehensive account is given of special sands and their utility in the various branches of the Ceramic industry. (From a Report presented to the U.S. Bureau of Mines).

ENGLISH AND AMERICAN CHINA CLAYS COMPARED.—J. W. Higman (*Chem. Age*, **12,** *China Rev. Sect.*, 8, March, 21, 1925). As the result of a visit of inspection to the U.S.A., H. states that English China clays are much superior in quality and lower in price in the industrial areas of America than the domestic clays.

THE MAGNESITE DEPOSITS OF MANCHURIA.—K. Niinomy (*Econ. Geol.*, **20,** 25, 1925). The crystalline magnesite deposits of southern Manchuria rival those of Hungary in thickness and extent. A geological account is given of the deposits. The magnesite is used in making refractory bricks and liquid floor cement. The dead-burned product contains 2·86% SiO_2, 4·32% Fe_2O_3 and Al_2O_3, 2·58% CaO, 88·92% MgO, 1·28 loss on ignition.

PREPARATION OF ARTIFICIAL SILLIMANITE FOR REFRACTORY USES.—C. E. Sims, H. Wilson and H. C. Fisher (*Chem. Tr. J.*, **75,** 419, 1924, from *Trans. Amer. Electrochem. Soc.*, Preprint No. 23, October, 1924). To attain the necessary high temperature, several preliminary types of furnaces were tried. That finally adopted consisted simply of a hollow steel shell placed on a silica brick foundation. Two 75 mm. graphite electrodes were suspended above the shell from water-cooled holders, which were insulated from each other. Much trouble was experienced in melting the clay, which, however, was reduced to sillimanite by eliminating the silica. Artificial sillimanite crystallises in two distinct forms. The first has a vitreous

lustre and a conchoidal fracture, whilst the second is stony and almost microcrystalline. The former gave disappointing results, whilst the latter exhibited excellent refractory properties in comparison with silica and magnesite bricks. The chemical composition of artificial sillimanite is represented by the formula: $3Al_2O_3.2SiO_2$, differing in this reapect from the natural product. The most dangerous impurity is lime. If present to the extent of more than 1·5 per cent., it lowers the fusion point seriously.

THE MATTAGAMI CHINA CLAY DEPOSITS.—(*Can. Chem. Met.*, **8**, 266, 1924). The deposits occur along the Mattagami river in Ontario. Of the two which have been tested, the one contains china clay to a depth of 75 ft.; the clay analyses as follows:—SiO_2 49·5%, Al_2O_3 35·79%, Fe_2O_3 0·13%, CaO slight trace, MgO slight trace, loss 13·85%. A second deposit has an admixture of very pure glass sand, of the composition:—SiO_2 99·1%, Al_2O_3 0·324%, Fe_2O_3 0·176%, CaO and MgO traces. The geology of the deposits is discussed briefly.

A VALUABLE COLLOIDAL CLAY.—H. S. Spence (*Chem. Tr. J.*, **76**, 35 1925). The properties and uses of Canadian bentonite are described. Analyses of 10 varieties from different parts of Canada are given. Silica, alumina, and water, in the proportion: 61 : 18 : 10 (mean of 15 analyses) make up about 90% of the material. Bentonite is a stratified clay, formed by the alteration of volcanic ash.

PHYSICAL AND CHEMICAL PROPERTIES, TESTING, ETC.

THE DEAD-BURNING OF DOLOMITE.—I.—J. T. Robson and J. R. Withrew (*J. Amer. Cer. Soc.*, **7**, 61, 1924). When made into bricks, dolomite, having the theoretical formula $CaCO_3.MgCO_3$, has the undesirable property of disintegrating when allowed to stand in the air, due to the slaking of the lime content. Since dolomite is very abundant and possesses great refractoriness, together with basic properties similar to the more expensive magnesite, work was carried out to obtain dolomite in the dead-burned form, and to investigate the feasibility of producing bricks with this material. In this introductory paper, the first of a series, the work of previous investigators is reviewed, the following conclusions being drawn: (1) Kaolin as a fairly effective flux for dead-burning dolomite; (2) many different compounds and eutectic mixture are capable of forming among the five components CaO, MgO, Fe_2O_3, Al_2O_3, and SiO_2; (3) CaO may combine with Fe_2O_3 and act as a solvent for lime; (4) the presence of Fe_2O_3 is essential to dead-burn MgO to the stable from periclase; (5) lime becomes inactive to water on being calcined in the presence of silica and silicates; (6) the more MgO present in a lime, the slower will it slake.

FUNDAMENTAL FACTORS IN THE USE OF POTTERY PLASTER.—U.S. Gypsum Co. (*Cer. Ind.*, **4**, 216, 1925). The occurrence, preparation, physical and chemical properties are outlined briefly. The troubles which occur most frequently in the use of plaster moulds in potteries are enumerated, their causes diagnosed, and remedies or preventatives prescribed.

LIMESTONE FOR SHEET GLASS MAKING.—E. P. Arthur (*J. Amer. Cer. Soc.*, **8**, 125, 1925). Drawn sheet glass demands greater purity of raw material than other ordinary types. The limestone used must, when ground, be entirely free from foreign matter, such as chert, overburden debris, etc. Hence, the chemical composition alone does not constitute a reliable basis for specification purposes. A careful system of selection in the quarry itself is essential. The usual method of taking representative samples in testing the raw material for contamination is useless, since a very small percentage of foreign matter *e.g.*, clay, in a truck load of ground stone, is sufficient to ruin a considerable quantity of sheet glass. Coarsely ground stone should be used if possible, since it is less likely to be contaminated.

THE PARTICLE ANALYSIS OF CLAYS BY SEDIMENTATION.—E. Schramm and E. W. Scripture (*J. Amer. Cer. Soc.*, **8**, 243, 1925). The work

of Odén and others on the particle analysis of fine-grained materials by sedimentation is reviewed and the method is applied to clays in the dispersed state to determine quantitatively the distribution of the particles. No special apparatus was used, the accumulation curves for ball clays and refined kaolins being determined with sufficient accuracy by the use of a set of test tubes and a wooden rack. Valuable data regarding the condition of a clay were obtained by sedimentation without the use of a deflocculating agent. Flocculated clays are of a gelatinous nature; hence Stoke's law is inapplicable in this case. The results of the particle analyses, which were confirmed by microscopical observations, were correlated with other properties of the clays. The completely dispersed and fine-grained clays exhibited the highest shrinkage and dry strength. The latter property increased as the result of deflocculating the clay.

STUDIES ON THE DOLOMITE SYSTEM.—H. L. J. Bäckström (*J. Chem. Soc.*, **125**, 430, 1924). A discussion of Mitchell's paper (*c.f. Trans.*, **22**, 73 and 103 Abs., 1923).

PLASTICITY. I.—O. Ruff (*Zeits. anorg. Chem.*, **133**, 187, 1924). The subject of plasticity is discussed from the theoretical standpoint. The plasticity of a substance or mixture depends upon the possibility of permanently displacing molecular layers or complexes without disrupting them. It is a function of deformation capacity and cohesive strength. The resistance to displacement is explained by the internal friction.

PLASTICITY II.—PLASTIC BODIES CONTAINING ZIRCONIA.—O. Ruff and J. Moczala (*Zeits. anorg. Chem.*, **133**, 193, 1924). The conditions under which zirconia can be converted into a plastic state, and the working method for producing therewith ceramic objects, particularly crucibles for high-temperature work, by the ordinary casting process, have been determined. With pure water, the pure oxide, even when ground to particles $0{\cdot}5\mu$ in size, is not sufficiently plastic for practical purposes. The development of plasticity requires a modification of the surface conditions of the particles, by treatment either with fused alkalis or with dilute acids. Active groups of atoms are thus formed on the surface; these are the direct cause of the plasticity in the first case, but in the second, further acid treatment is necessary. The second case appears to support the hypothesis that a positive electrical charging (ionisation) of the particles, and the consequent formation of a film of water, is the final cause of plasticity. The minimum temperatures for the preparation of the oxides from zirconium salts were determined, and also the more important ceramic properties of zirconia. Small crucibles were cast, fired to different temperatures, and tested for shrinkage, porosity, etc. Excellent ware, with a thin yet dense body and highly resistant to high temperatures, can be prepared, if the correct conditions regarding choice of oxide, slip, strength, and temperature are observed. Other refractory oxides (alumina, thoria, yttrium oxide, etc.) can be added to reduce the porosity and lower the firing temperature without seriously affecting the resistance to high temperatures. Crude zirconium ore can be used in place of the pure oxide, the upper limit of serviceability depending upon the kind and quantity of impurities present. Articles made therefrom can be used up to a temp. of about 1,600°.

POROSITY III. PLASTIC BODIES WITH ALUMINA.—O. Ruff and W. Goebel (*Zeits. anorg. Chem.*, **133**, 220, 1924). The conditions for rendering alumina plastic were studied similarly to zirconia (above), and were found to be of a like nature: finely dispersed condition and surface activation (acid adsorption). A coagulation value of the acid contration for the slips could not be determined.

THE ACTION OF FLUXES ON FINE-CERAMIC RAW MATERIALS.—K. G. Vershofen (*Keramos*, **3**, 451, 1924; *Chem. Zentr.*, **96**, I., 1360, 1925). The effect of strongly basic calcium, magnesium, and sodium compounds, and also of soluble fluorides, upon the four chief raw materials—clay, kaolin,

felspar, and quartz,—at temperatures up to 1,000°, was studied. The first two had no effect, whilst felspar was practically indifferent. Quartz was the most effective, but its action is dependent upon the degree of fineness of the particles.

II.—MANUFACTURING PROCESSES :

GENERAL.

Patents.

VITRIFIED PRODUCT.—A. de Gallaix (*U.S. Pat.* 1,523,179, 13/1/25). A mixture consisting essentially of powdered slag, powdered grog, and plastic clay is burned to a temperature sufficiently high to produce complete vitrification. The product is impervious to water, oil, and grease, is unaffected by frost and atmospheric conditions, and is highly resistant to shock.

DRY SATIN WHITE AND PROCESSES OF MAKING SAME.—H. V. Dunham (*U.S. Pat.* 1,523,182, 13.1.25). A mixture is prepared by adding to satin white paste any water-soluble substance having the property of causing the dried product, on mixing with water, to assume the condition of a smooth paste free from hard lumps and grains. The mixture is then dried.

COMPOUNDING AND PREPARATION OF BODIES, ETC.

THE PREPARATION OF REFRACTORY VESSELS WITH ZIRCONIA.—O. Ruff and G. Lauschke (*Cer.*, **27**, 1, 1924). Crucibles were prepared of pure zirconia, and of mixtures of 100 parts of this material with 1, 3, and 6 parts of silica, glucina, magnesia, alúmina, thoria and yttria, in addition to mixtures of raw and pure zirconia. Starch was used as the bonding medium. The figures for shrinkage, percentage variation in weight, and porosity are given in tables. The figures indicate that porosity, like shrinkage is dependent on the temperature to which the body has been fired. The crucibles made of pure zirconia do not crack when fired to 2,000°. They commence to crack slowly at 2,200°, and rapidly at 2,400°. The addition of silica and magnesia increases the tendency to cracking, whilst glucina, thoria and yttria exert only a moderate influence in diminishing this tendency. On adding 3 parts of alumina, the tendency to rupture is decreased, and with 6 parts it is eliminated entirely. The crucibles made with this mixture withstand a temperature of 2,400° without perceptible change in form. The variations in weight, indicated above, are due to three causes : (1) The reduction of the zirconia in the reducing atmosphere of the furnace ; (2) the volatilization of the added substances ; (3) sublimation of the zirconia, magnesia, glucina and silica are the most volatile of the oxides ; even at 2,000° a considerable proportion has volatilized, and at 2,400° it reaches 90 to 95 per cent.

The experiments showed that, starting with zirconia as a base, it is possible to produce dense objects by adding suitable oxides and by firing in a special furnace. Finely powdered zirconia appeared to be most suitable, and the oxides most favourable as additions were alumina, thoria and yttria. If it is desired to fire to 2,000°, it is preferable to add 1% alumina ; to 2,200°, 1% thoria ; and to 2,400°, 1 to 3% yttria. Further additions merely serve to increase the porosity. The oxides of glucinium and of magnesium, employed in small quantity, diminish porosity. Silica acts in a deleterious manner. For temperatures up to 1,900°, raw zirconia may be employed. Above that, the crucibles are not stable ; the silica, which they contain, volatilizes, rendering them porous and unfit for use.

AMERICAN CLAYS AS COMPARED WITH ENGLISH CLAYS IN WHITE WARE BODIES.—E. H. Fritz (*J. Amer. Cer. Soc.*, **8**, 253, 1925). American clays were substituted for English clays in an ordinary plastic body, comparative results being thus obtained. English ball clays vary much more than the American, especially in plasticity, whilst English china clays

are inferior as regards bonding strength and plasticity to the best Georgia kaolin. English ball clays, however, have a lower vitrification temperature than the corresponding American clays. Some English china clays are superior to all others as regards firing colour. The body developed entirely from the best American clays equalled in quality the English clay bodies, the higher vitrification point of the ball clays having apparently no adverse effect at a firing temperature of cone 10.

THE MAKING OF DOLOMITE BRICKS AND A STUDY OF THEIR PROPERTIES. I.—A. I. Andrews, G. A. Bole and J. R. Withrow (*J. Amer. Cer. Soc.*, **8**, 84, 1925). The use of compositions suggested in previous work (*J. Amer. Cer. Soc.*, **7**, 61, 141, 207 and 300, 1924), the effects of the firing temperature upon the properties of dolomite bricks, the advantages and disadvantages of various binders, and the properties of the bricks relative to their serviceability were studied. Various mixtures of dolomite and fluxes (ferric oxide, alumina, and silica) were ground thoroughly and made up into briquettes, which were fired, cooled, and then ground to pass a 20-mesh sieve. Bricks were prepared from this ground material by the use of different binders. The most favourable results were obtained with 200-mesh dolomite mixtures calcined to cone 20, the mixtures being: 9–0–6M (9% Fe_2O_3 . 0% Al_2O_3, 6% SiO_2, 85% dolomite); 6–3–6M, and 2–4–4M. The only suitable binders were molasses, sodium silicate, and dextrin. The best bricks were made by using 20-mesh D9–0–6M composition (above mixture ground to 200-mesh and calcined to cone 20, plus 13% of a 1: 3 dextrin-water mixture as binder) and 20-mesh S6–3–6M (12% of a 5% sodium silicate solution as binder). The bricks were fired to cones 18 and 16 respectively, and were dense, well-shaped and refractory. The cone fusion temperatures of mixtures 9–0–6M, 6–3–6M and 2–4–4M, determined in a specially constructed oxyacetylene furnace, were above cone 40 (2,010°). Bricks D9–0–6M and S6–3–6M, when held at 1,350° for 1 hr. under a load of 25 lb. sq. in., showed a compression of 3 and 0·9% respectively, with no tendency to crack or squat. Both, however, spalled characteristically when heated to 1,350° and subsequently cooled a room temperature.

MANUFACTURE OF DOLOMITE BRICKS AND A STUDY OF THEIR PROPERTIES. II.—A. I..Andrews, G. A. Bole, and J. R. Withrow (*J. Amer. Cer. Soc.*, **8**, 171, 1925). The squatting of bricks of the composition 2-4-4M, with molasses as a binder, was found to be due to the brick material itself, and not to a flowing or softening of the glux or molasses. In the search for suitable binders, water, carbonated water, Bindex, two grades of tar, and Epsom salts were tested, but for standard size bricks sodium-silicate solution and the dextrin—water mixture gave best results. Finely ground calcined dolomite mixtures showed a much greater tendency to slake when exposed to the atmosphere, than coarsely gronnd material. In the dead-burning of dolomite, neutral or basic refractories must be used (magnesite or chromium), since dolomite fluxes readily with refractories of an acidic nature. The use of less flux was unsuccessful, because material thus prepared slaked more readily. Talc proved to be unsatisfactory when used as a flux in the dead-burning process.

Patents.

PREPARATION OF CERAMIC PRODUCTS.—W. Vershofen (*German Pat.* 403,175, 28/7/23). Addn. to G.P. 371,593. In addition to fluorides, calcium salts are added to the clay. Complete softening of the body is thus avoided.

REFRACTORY COMPOSITION.—A. L. Sherman, Assr. to Anthracite Refractories Co. (*U.S. Pat.* 1,521,719, 6.1.25). A refractory composition consists of a mixture of reburned coal ashes and anthracite clay.

HIGHLY REFRACTORY MATERIAL.—H. H. Buckman and G. A. Pritchard (*U.S. Pat.* 1,521,749, 6.1.25). The material contains carbon in a permanent, graphitic form and also a chemical compound of natural zircon.

CERAMIC BODIES; INCREASING PLASTICITY.—J. H. Beaumont (*Engl. Pat.*, 224,257, May 1, 1923). To increase the plasticity of ceramic bodies, refractory mixtures, mortars, etc., comprising kaolin, clay, bauxite, flint, asbestos, calcium carbonate, etc., a small proportion (5-20%) of a highly colloidal earth, such as bentonite, ehrenbergite, damonterolite, montmorillonite, is added, either as a fine powder, or mixed with water, or as a gelatinous mass produced by the addition of a solution of alum, sodium silicate, etc.

REFRACTORIES CONTAINING GRAPHITE, CLAY, ETC.—H. Wade (*Engl. Pat.*, 223,986, 31 July, 1923). Hollow refractory containers are made from a mixture containing graphite and a ceramic bond each in excess of 15%, *e.g.*, 15-65 parts of graphite, 15-20 parts clay, and 5-15 parts siliceous material are mixed and burned until the bond is vitrified, *i,e,*. to at least 1,093°. Other refractory materials such as alumina, silicon carbide, zirconia, may also be added.

SEMI-PORCELAIN BODY FOR THE MANUFACTURE OF POTTERY.—J. E. Tams (*Engl. Pat.*, 228,058, 5 June, 1924). A mixture of ball clay (8 parts), china clay (12 parts), ground flint (12 parts), and hydrated magnesium silicate powder (3 parts) is blunged with water into a casting slip or into a clay to be pressed, etc., in the usual way. Superior earthenware which will not craze can be produced [Note: According to *Brit. Pat.* 713, 21 March, 1859, "talc,—or other silicates of magnesia,—in powder, or mixed with glass, felspar, lime, or alumina, as pressed in moulds and baked, burnt, or fired."—In two letters of Dr. Pococke, dated 13 Oct. and 2 Nov., 1750, it is stated that "soapy rock," found near Lizard Point, is used at Bristol for making porcelain].

REFRACTORY SUBSTANCES.—Morgan Crucible Co., Ltd., and P. Lindsay (*Engl. Pat.*, 227,270, 17 Dec., 1923). Crucibles, etc., are prepared from mixtures such as: 30% crystalline graphite, 20% clay, 10% sand, 10% silicon carbide, and 30% $Al_2O_3.SiO_2$.

REFRACTORY FIREBRICKS, CRUCIBLES, ETC.—F. W. Cobb (*Engl. Pat.*, 230,248, 22.2.24). Firebricks, crucibles, etc., are moulded from a mixture of one part of fireclay, two parts of ground (20-mesh) pebble, or, alternatively, 3 parts of fireclay, 4 parts of ground pebble, and one part of ground tessara. The natural pebble, obtained from sand beds, consists mainly of quartz pebbles together with limestone, volcanic ash, and sandstone pebbles.

SHAPING, MOULDING, DRYING, ETC.

PATENTS.

IMPROVED PORCELAIN CRUBICLES.—Staatliche Porzellan-Manufaktur (*Engl. Pat.*, 220,618, 5 Aug., 1924) .A porcelain crucible intended as a substitute for the Gooch crucible in analytical work, has a bottom of finely porous material which is fired on to the porcelain mantle. The bottom is formed of a mixture of 80% kaolin and 20% fireclay of stated composition.

MOULDING SILICA BRICKS, ETC.—Refractories Machinery Manufacturing Co. and C. L. Norton (*Engl. Pat.*, 226,053, 15/1/4). Moulded refractory shapes are formed by allowing the granular material to fall in a dense stream into an open-bottomed mould box, temporarily closed by a pallet. The mould is subsequently removed, leaving the mould shape on the pallet, where it is dried. The pallet may be coated with oil to prevent adhesion. The apparatus for carrying out the operation consists of endless-chain machines, presses, cleaning apparatus, etc.

KILNS, OVENS, MUFFLES; FIRING TECHNIQUE, ETC.

REFRACTORIES FOR BOILER FURNACES.—L. Litinsky (*Feuerung*, **13**, 70, 1925). For most types of stationary steam boiler furnaces, at least two, and frequently three kinds of bricks are required: (1) bricks with which the burning coal comes into direct contact; (2) those which are reached by

the hot gases and flames ; (3) bricks which come into contact with hot gases only. Bricks for boiler furnaces have to satisfy certain requirements with regard to resistance to high temperatures, mechanical usage, temperature changes, volume changes and chemical action. In the more exposed parts of the furnace, where the bricks are in direct contact with the hot gases and flames, they should possess refractory properties corresponding to cone 31-33, in other parts of the furnace cone-26 bricks may be used. The requirements for the different kinds of furnaces are : (1) For ordinary furnaces, melting temperature 1,580°C. minimum ; linear expansion or contraction after heating for 3 hours at 1,300°, 1% maximum ; cold crushing strength 1,420 lb. per sq. in minimum ; (2) mechanical draught (undergrate) furnaces : melting point 1,650° ; linear expansion or contraction after 3 hours' heating at 1,500°–1·5% maximum ; cold crushing strength 1,420 lb. per sq. in. minimum ; maximum water absorption 14% of the dry weight; (3) For locomotive furnaces. As under (2), except that the minimum cold crushing strength should be 1,770 lb. per sq. in ; (4) For furnaces fired with liquid fuels, or draught furnaces working at exceptionally high temperatures. Melting point at least 1,710° ; linear expansion or contraction after heating for 3 hours at 1,600°–1·5% maximum ; minimum cold crushing strength 1,420 lb. per sq. in. ; maximum water absorption 15% of the dry weight.

ADAPTATION OF TUNNEL AND CAR KILNS TO FIRING REFRACTORIES.—P. Dressler (*J. Amer. Cer. Soc.*, **8**, 43, 1925). In firing heavy and large fireclay shapes, such as are required in the glass industry, the chief requirement is a perfectly uniform, slow and controlled firing combined with a period of uniform temperature sufficiently long to ensure penetration through the pieces. Abrupt changes of temperature must be eliminated entirely. The muffle type of kiln would best meet the requirements. The direct-fired kiln with longitudinal draught is best suited to the firing of ordinary fireclay bricks, which require a temperature not exceeding cones 14-16. The chief problems have been to construct a kiln capable of handling a sufficiently large tonnage, and in securing a uniform distribution of heat in the kiln. This type of kiln would not be suitable for firing high temperature refractories such as silica, magnesite, chrome, etc., which necessitate long periods of heat treatment. Here, again, rapid fluctuations of temperature would be fatal. To meet all these requirements a kiln having a much greater cross-section and yet permitting an even distribution of heat has been developed. In the cross Fire Regenerative Kiln the gases pass transversely from side to side, and not longitudinally from the centre outward. Two advantages arise from this : (1) The heating medium traverses only one zone ; hence, each section can be regulated independently ; (2) Trucks of much greater width can be used, since the hot gases are forced through the centre of the trucks and not merely in a longitudinal direction between walls and ware. A number of burners are fitted on both sides of the kiln and are used alternately, the draught being switched from side to side at intervals. Under these conditions the waste heat cannot be applied to preheat the ware ; it is, therefore, stored in regenerators and recovered by preheating the air and the fuel when the direction of flow is reversed. The kiln consists of a number of short sections, about 12′ 6″ long, each of which has its own independently regulated fuel and air supply. It can be constructed in two different ways : (1) with two trains of cars passing through in opposite directions ; (2) with a single train of cars. The chief advantage of the cross-fired regenerative kiln is, that it permits the production, on a long cycle, of a sufficient volume of ware without extending the kiln to an inordinate length. The temperature attainable is limited only by the failure point of the refractories of which the kiln is built. Any desired atmospheric conditions can be maintained in any of the independent sections, and complete control of every step of the firing and cooling is secured.

THE FIRING OF REFRACTORY PRODUCTS IN FRANCE.—R. V. Widemann (*J. Amer. Cer. Soc.*, **7**, 29, 1924). For firing refractories, the

French favour the continuous kiln, with the products stationary, and the fire moving. In some cases the fuel is delivered mechanically directly into the interior of the kiln. Intermittent kilns are found only on small works, or for firing special products. The tunnel kiln, with products moving and fire stationary, is of great interest economically. Although one of the first kilns of this type—the Faugeron kiln—originated in France, where interesting results were obtained, tunnel kilns for firing refractories are still scarce and are all of recent construction.

Coal may be utilised as fuel in three ways : (*a*) by direct combustion ; (*b*) by direct gasification ; (*c*) by preliminary distillation, more or less complete, and utilisation of the combustible residue according to (*a*) or (*b*). A certain success has been attained in France by direct combustion of powdered coal, which affords the possibility of simplifying the mechanical installation. Direct gasification has had great success, but this system is now losing ground. The present tendency is to use gasifiers only when the coal is of poor quality or contains elements which might affect the product.

SOME FUNDAMENTAL PRINCIPLES GOVERNING THE CORROSION OF A FIRECLAY REFRACTORY BY GLASS.—R. B. Sosman (*J. Amer. Cer. Soc.*, **8**, 191, 1925). The subject is treated by a method similar to that followed in the author's paper "The Physical Chemistry of the Seger Cones" (*Trans. Amer. Cer. Soc.*, **15**, 482, 1913). Consideration is first devoted to the fundamental physico-chemical principles involved, *e.g.*, entropy, energy, and thermo-dynamical potential, the importance of the last-named being emphasised in dealing with the corrosion of a glass pot. The conception of "equilibrium" is illustrated by a consideration of the interaction between a simple type of refractory and a molten glass within a well-defined "system" at the boundary of pot and glass. The rate of the chemical reaction, *i.e.*, the time required to reach a state of equilibrium between the constituents of the refractory and the liquid glass, is the most important factor in a study of corrosion. It is modified by certain other factors, *e.g.*, diffusion, because the molecules of molten glass diffuse more slowly through a highly viscous fluid than through one of low viscosity. Since silica dissolved in glass raises its viscosity, the solution by the glass of the refractory wall tends to produce a protective layer of highly viscous material near the pot wall. The addition of "mineralisers" lowers the viscosity ; hence the addition of fining agents to the molten glass is a matter of importance to glass makers. Mechanical factors also influence corrosion. A steady flow on the molten glass minimises wear by producing a steady gradient of pressure, whilst turbulent flow increases wear by bringing more of the glass into contact with the refractory walls. A refractory of porous texture presents a larger surface to the corrosive action of the molten glass than one of a dense structure. Nevertheless, rapid and uniform corrosion may possibly be preferable to slow corrosion, which produces stones in the glass.

THE THERMAL CONDUCTIVITY OF REFRACTORY MATERIALS.—P. Gilard. (*Revue universelle des Mines*, **4**, 34, 1924). A full review of recent literature on the subject is given and a bibliography is included. The conductivity data obtained by Horning, Dougill, Hodsman and Cobb, Green, Bucher, Wologdine, etc., on various refractories are tabulated.

FIRING POTTERY WITH GAS.—(*Chem. Age, China Rev. Sect.*, **12**, 9, Feb. 21, 1925). An account is given of an experiment which is being conducted at Plymouth, where pottery is being made, on a small scale, and fired in a gas-kiln.

STANDARDISATION AND INDUSTRIAL RESEARCH IN THE REFRACTORY MATERIALS BRANCH.—F. Kanhäuser (*Ker. Rund.*, **33**, 101, 1925). The subject is discussed with reference mainly to American and British standards. The German Admiralty Specifications of 1908 are quoted and discussed.

DESIGN AND OPERATION OF HOT GAS PRODUCER PLANTS.—

W. S. Mayers (*Glass Ind.*, **6**, 1, 1925). The subject is discussed from the practical point of view, hints being given on the general design, location, the dust problem, handling coal and ash, fuel storage, etc., in connection with producer plants.

CLASSIFICATION OF FUELS BY RATIONAL ANALYSIS.—C. Blacher (*Feuerung*, **13**, 86, 1925). The hydrocarbon content of the volatile ingredients is calculated from the oxygen content and the content of volatile matter. This factor, together with the volatile content, determines the behaviour of the fuel in practice. In a scheme based on these values, other factors, such as hygroscopic water content, specific gravity, maximum gasification temperature, calorific value, etc., are easily incorporated.

NOTES ON HEAT ECONOMY IN ENAMEL WORKS.—F. S. (*Ker. Rund.*, **33**, 103, 1925). Methods of recuperating heat in enamel kilns are described, *e.g.*, the Hermannsen and the Pitsch systems.

THE DIRECT-FIRED TUNNEL KILN ON ROOFING TILES.—C. R. Minton (*J. Amer. Cer. Soc.*, **7**, 821, 1924). A description is given of the Harrop tunnel kiln, installed for firing roofing tiles by the Pressed Brick Co. of Los Angeles. Length of kiln 325 ft., width 4 ft. 10 in., setting height 4 ft. 11 in. The kiln holds 52 cars, each carrying 766 pieces, or 2·3 tons of ware. There are five combination oil and gas burners on each side of the tunnel. Special features are a watersmoking device and two oxidation furnaces. The kiln is arranged at right-angles to the tunnel of a waste-heat dryer. The maximum temperature is 993°, and ware is drawn at 204°. The bottom of the kiln shows a tendency to become hotter than the top. A fuel saving of over 64% over round down draught kilns is obtained, and in setting and drawing labour of 29% and 46% respectively. A temperature chart is reproduced.

BRICKS FOR IRON AND STEEL FURNACE LADLES.—(*Brit. Claywr*, **33**, 231, 1924). The essential qualities of a good lining material for ladles are : (1) it must be highly refractory, since the metal entering the ladle may be at any temp. below 1,700° ; (2) it must be very strong at high temperatures to resist the great weight of molten metal ; (3) it must be resistant to abrasion ; (4) it must not be sensitive to sudden changes of temp. ; (5) it must be constant in volume to prevent shrinkage cracks. The properties of the different materials used are discussed, *e.g.*, fireclay, silica, sillimanite, magnesia, plumbago, zirconia.

AN ADIABATIC METHOD FOR STUDYING SPONTANEOUS HEATING OF COAL.—J. D. Davis and J. F. Byrne (*J. Amer. Cer. Soc.*, **7**, 809, 1924). An adiabatic calorimeter is described (with sketch). Time-temperature curves for different coals are given. Spontaneous heating of coal is an increasing function of the temperature. From an empirical formula it is concluded that no heating will take place below 26·27°C. and that Pittsburgh coal requires 144 hours to heat from this temperature to ignition.

Patents.

TUNNEL KILN AND METHOD OF OPERATING SAME.—L. Wilputte, Assr. to American Dressler Tunnel Kilns, Inc. (*U.S. Pat.* 1,522,166, 6.1.25). The products of combustion of gaseous fuel are caused to move through the chamber of a tunnel kiln in a direction approximately horizontal and transverse at all points to the length of the kiln (*c.f.* p. 7).

OPERATION OF SHAFT FURNACES.—G. Ködder (*German Pat.* 403,310, 21.9.23). The fuel is introduced into the furnace in combustible containers, the sides of which, one above another, form a column, which is surrounded by the charge. This fuel column extends the full height of the kiln. The containers may be fitted with bottoms which serve to break up the column into a number of sections. The ash remains in the centre, and does not contaminate the charge—cement, lime, gypsum, etc.

FIRING PORCELAIN IN THE UPPER CHAMBER OF ROUND KILNS.—P. Rosenthal (*German Pat.* 402,981, 25.6.22). The hot air from the lower (cooling) chamber is mixed with water vapour and passed below the grates of the fireboxes built in the side walls of the upper chambers. Water gas is thus formed.

IMPROVEMENTS IN ANNULAR FURNACES OR KILNS.—Woodall, Duckham & Jones (1920) Ltd., and Sir A. M. Duckham (*Engl. Pat.* No. 218,343, Feb. 2, 1923). The invention relates to annular tunnel kilns of the type in which the goods (bricks, etc.), to be heated are carried on a rotating annular support forming the floor of the kiln, and in which the hot gases are admitted to travel in the opposite direction to the ware in one section of the tunnel, while the goods are cooled in another section, by air moving in the other direction to the place of combustion. Methods are indicated for improving the construction, arrangement or operation of such kilns, mainly with a view to overcoming the difficulty of heating all the goods to the same temperature.

REFRACTORY CEMENT.—Soc. d'Etude des Agglomérés (*Engl. Pat.*, 224,214, 15 Oct., 1924). A refractory cement contains powder, obtained by crushing agglomerated zirconium ore, zirconium oxide, an organic binder (dextrin) and an inorganic binder (boric acid).

TUNNEL KILN.—Th. Larsson (*U.S. Pat.*, 1,517,437, 2 Dec., 1924). The temperature curve of the cooling zone is varied by drawing air through adjustable air openings spaced longitudinally in that zone.

HEAT INSULATING COMPOSITIONS.—H. W. H. Schnell and Schnell & Schellings Patenten (*Engl. Pat.*, 224,802, 10 Apr., 1924). Plaster of Paris is added to a froth obtained by heating a mixture of air-slaked lime and a soap solution or an aqueous solution of fat or oil; *e.g.*, 1 part by weight of plaster, 2 parts of lime, and 3 parts of a 1% soap solution. The product is porous and may be cast into blocks, etc., or it may be cast and then ground to powder, mixed with chalk and fibres and made into insulating cord.

BASIC REFRACTORY MATERIAL.—A. L. Brown, Assr. to The Standard Lime and Stone Co. (*U.S. Pat.* 1,527,347, 24 Feb., 1925). A basic furnace-lining material is formed by heating a mixture of dolomitic limestone, 2·5 to 5·0% iron oxide, and 0·5 to 2·0% felspar to a temperature above the melting point of the felspar.

APPARATUS FOR DRYING CHINA CLAY AND ARGILLACEOUS MATERIALS.—C. A. Battiscombe (*Engl. Pat.* 229,527, 22 April, 1924). The floor of a drying kiln is formed of a series of shallow, approximately square metal pans, supported on the flue walls so that the bottom plates are in direct contact with the products of combustion. The upper surface of the kiln floor is formed of fireclay tiles, placed side by side to cover the whole area of the bottom of the pans. The clay is placed on the tile floor, the pans being closed by a sheet metal cover. Means are provided to give air-tight joints, and thus permit the formation of a partial vacuum within the pans by the action of an exhaust air pump. More efficient drying is thus attained by the application of moderate heat.

REFRACTORY CEMENT WITH A BASE OF ZIRCONIUM ORE.—Soc. d'Etude des Agglomérés (*Engl. Pat.* 224,214, 12 Feb., 1925). The mixture is formed of 30 kg. of almost pure zirconia, 0·4 kg. of an organic binder (dextrin), 0·2 kg. of an inorganic binder (boric acid), and 100 kg. of powder obtained by crushing agglomorates of zirconium ore, which has been subjected to prolonged baking, heated rapidly to 2,500°, and then discharged into a stream of cold water.

TUNNEL KILN.—Woodall-Duckham Ltd. and A. M. Duckham (*Engl. Pat.*, 228,987, 12 Feb., 1925). A straight tunnel kiln is constructed similarly to the annular kiln discribed in *Spec.* 212,585 (TRANS. **23**, 42A, 1924). It comprises continuous drying, heating and cooling zones, with suitably arranged flues. The floor consists of separate, movable sections, air being prevented

from entering from beneath the floor by means of sand troughs and trough-shaped extensions carried by the sections. Loss of heat by radiation is minimised by means of longitudinal flues in the side walls and roof of the kiln. Means are provided for preheating secondary air for combustion, and for recuperating waste heat from the different sections.

REFRACTORIES FOR CRUCIBLES, LADLES, ETC.—P. Guillaume (*Engl. Pat.* 226,184, 25 Nov., 1924). The stoppers and linings of the outlets of crucibles and ladles used in casting manganese steel are made of a mixture of pipeclay and magnesite.

SYNTHETIC REFRACTORY MATERIALS.—J. F. Mollen and W. T. Patnoe (*U.S. Pat.* 1,525,655, 10 Feb., 1925). Refractory products are formed of raw dolomite mixed with small percentages of argillaceous matter and common salt, and calcined. The salt is almost eliminated during calcination and the final product is composed of approximately 85% of lime and magnesia, and 14% of argillaceous matter.

ANNEALING FURNACE AND LEHR.—W. C. Ansler (*U.S. Pat.* 1,533,298 14.4.25). The heating chamber of a lehr of the muffle type is so constructed that ware can be introduced at the side of the muffle. The hot gases circulate round the chamber to the rear of the side inlets. The muffle chamber contains an endless conveyor supported on wheels, the portion of the chamber into which the wheels extend being heated by a system of flues and passages for hot air.

WASTE HEAT COOLING SYSTEM FOR PERIODIC CLAY-BURNING KILNS.—R. L. Ash (*U.S. Pat.* 1,533,999, 14.4.25). A verticle flue is constructed inside the kiln and adjacent to the wall. The upper end of the flue is open near the top of the kiln, whilst a passage leads from the bottom of the flue to a waste heat tunnel. This passage has a port outside the kiln and contains an adjustable damper between the port and the tunnel, and a false wall between the port and the flue.

(SILLIMANITE) REFRACTORY PRODUCT, AND METHOD OF PRODUCING IT.—H. P. Hood, Assr. to Corning Class Works (*U.S. Pat.* 1,527,874, 24/2/25.) Sillimanite is ground to a fine powder, mixed to a paste with water, shaped, and fired to sintering point.

GLAZES, ENAMELS.

EXPERIMENTS IN THE PROBLEM OF THE TURQUOISE ALKALINE GLAZE.—M. M. French (*J. Amer. Cer. Soc.*, **6**, 405, 1923; **8**, 143, 1925). The object was to produce an insoluble turquoise blue glaze, which would render the ware impervious to water. Experiments were made with the following bodies :—

	No. 3	No. 4	No. 5	No. 6	No. 8	No. 10	No. 11	No. 12
Cornwall stone	—	—	17	—	—	—	—	—
Ball clay (Tenn.)	18	14	17	13	18	18	28	28
Felspar ..	10	19	—	—	14	10	—	—
Kryolith ..	8	8	6	6	6	—	4	—
Georgia clay	—	—	—	19	—	—	—	—
Flint ..	64	59	60	62	62	64	68	68
Whiting ..	—	—	—	—	—	8	—	4

The glaze applied to the raw, dry bodies was :—

$$\left.\begin{array}{ll} Na_2O & 0{\cdot}6 \\ K_2O & 0{\cdot}1 \\ Ca_2O & 0{\cdot}3 \end{array}\right\} SiO_2 \quad 2{\cdot}8$$

The best blue colour was obtained by adding from 6 to 12 grams of black copper oxide to the batch. The colour was also dependent upon the

method of firing the glaze, and the type of biscuit body. No. 12 was an unsatisfactory body, but it gave the best blue colour. The glaze sometimes crazed on large pieces but not on smaller pieces. Promising tests are now being carried out with a raw body covered with a raw glaze compounded as simply as possible and fired to cone 04.

ENAMELLING DEFECTS DUE TO THE CAST IRON.—A. Malinovszky (*J. Amer. Cer. Soc.*, **8**, 72, 1925). Chemical analyses and microphotographs are given to show that carbon is intimately connected with the cause of blistering, lifting, and in some cases chipping. Blistering occurs if there is a high content of combined carbon in the iron and if temper carbon is present, whilst a low content of combined carbon and an even distribution of graphite carbon in very minute subdivision have no ill effects. An increase of carbon in the iron, due to the enamelling treatment, was observed, but is not explained. The analyses of the iron before and after enamelling also indicated changes in the combined carbon. Uniformity in the quality of the pig and scrap iron, and the use of a dense, strong type of coke, are important factors. Lack of uniformity in the thickness of the finished castings causes chipping, crazing, lifting, pin holes, etc.

A SIMPLE METHOD OF CONTROLLING ENAMELS.—L. Vielhaber (*Glashutte*, **54**, 138, 1924). Staley's work (*Trans. Amer. Cer. Soc.*, **12**, 502, 1911), has been simplified and developed. By means of a graph the melting temperatures can be read off directly. A table of "fusibility factors" for the usual batch ingredients is given, to be used in conjunction with the graph.

THE CHEMICAL RESISTANCE OF ENAMEL FRITS.—T. Schauer (*Spech.*, **58**, 5, 1925). The tests carried out to elucidate the problem were made on small enamel cubes, prepared in the usual way, which were boiled in different acids and alkali solution. The various melts were also examined in thin section. The resistance of the enamels to the chemical action of the reagents bears a direct relationship to the degree of dissociation of the latter. Unsuitable cooling has a bad effect on the chemical resistance. Dissociation or disintegration of the enamel, which may readily take place, increases its solubility. The resistance increases if the various ingredients of the enamel are themselves highly resistant to chemical reaction; or if ingredients are added which form highly insoluble compounds in the enamel.

THE DEVELOPMENT OF SOME JEWELLERY ENAMELS.—H. G. Wolfram and W. N. Harrison (*J. Amer. Cer. Soc.*, **7**, 857, 1924). A review of the literature is followed by an account of the technique of the subject. Thirty-three enamels, based on batch data supplied in the literature, were prepared; each of these consisted of a constant portion of 55 parts, viz., 20 silica, 30 lead oxide, and 5 sodium oxide, and a variable portion of 45 parts, the latter being formed of additions of oxides already contained in the constant part, or of other oxides. This arrangement facilitated a study of the effects produced by each component. Disintegration of the molten enamels was effected by pouring them on to a steel plate. The powdered enamels (80-mesh), were applied to shallow hollows in sheet copper, no bonding material being used. They were fired in an electric furnace to about 950°. Certain of the colourless enamels produced were taken as base fluxes for the preparation of coloured enamels, varying proportions of colouring media (metallic salts or oxides) being added. The results indicated that bubbles were most effectively eliminated by heating the enamel sufficiently to produce a very fluid melt. Grinding to pass an 80-mesh but retained on a 100-mesh gave the best results. All the successful enamels contained boric acid together with silica or lead oxide, or both, in the variable portion. Those having the highest ratio of lead oxide to silica were superior. Enamels containing potash appeared to be more satisfactory than those containing soda. The colouring agent affected the general appearance, gloss and texture.

PATENTS.

SALT-GLAZED STONEWARE FIRED IN GAS KILNS.—C. Roschmann (*Ger. Pat.* 401,359, 29 Nov., 1922). The salt is mixed with fuel and passed into the kiln through a nozzle. Hitherto, satisfactory salt-glazed ware had not been manufactured in a gas-fired kiln.

APPLICATION OF TRANSLUCENT COATINGS TO VITREOUS OBJECTS.—A. S. Cachemaille, Ass. to Westinghouse Lamp Co. (*Engl. Pat.* 230,643, 29/3/24). A suitable coating material, containing a soluble silicate, is applied to the object by means of a spray gun. Hot air may be used in the spraying operation, and the coating material may be heated before being sprayed on to a cool or preheated surface. The claim relates to the application of translucent coatings to electric lamp bulbs in particular.

PLANT AND MACHINERY, ETC.

CRUSHING AND GRINDING. PART I.—S. G. Ure (*J. Soc. Chem. Ind.*, **43**, 1,144, 1924). Various types and makes of machines are illustrated and described.

THE ORIGIN OF THE HARDINGE MILL.—J. C. Farrant (*Chem. Age*, **12**, 98, 1925). The first experimental tests were carried out in 1907 at a silver mine in Colorado. The first Hardinge mill measuring 6′ by 22″ was installed in 1908 at the Cobalt Central Mines, Canada. Rapid development followed.

DISINTEGRATING MILLS.—A. S. W. Jones (*Industrial Chemist*, **1**, 41, 1925). Colloid mills—Plauson, Premier and Hurrell types—are illustrated and described.

NEW MACHINES FOR TESTING BUILDING MATERIALS.—H. Hecht (*Tonind. Ztg.*, **49**, 289, 1925). Machines for testing the crushing strength of all types of building materials, and for determining the permeability to water are briefly described.

III.—FINISHED PRODUCTS: TESTING, ETC.

THE LABORATORY TESTING OF ALUMINOUS REFRACTORIES.—R. F. Giller (*J. Amer. Cer. Soc.*, **7**, 663, 1924). A preliminary investigation has been conducted on a number of refractories used in lining rotary cement kilns, and containing 50% of alumina or more. The samples, submitted by five manufacturers, consisted of two brands of fireclay refractories and eight brands of aluminous refractories, which were tested for softening point, constant volume, quenching, absorption, deformation under load, and slagging. The data obtained indicated that, with refractories containing 50%, or more, of alumina, the following results may be expected from laboratory tests :—(1) The softening point is equal to, or exceeds, that of the Orton standard pyrometric cone 34 ; (2) The constant volume test does not give results of value ; (3) The refractory withstands 18 or more quenchings without failure ; (4) The absorption, does not satisfy specifications, although generally higher than for refractories containing less than 50% of alumina ; (5) The deformation does not exceed 5% with a load of 25 lbs. per sq. in, and a maximum temperature of 1,450°C. ; (6) The softening point of a mixture of equal parts of refractory and cement clinker equals, or exceeds, that of the Orton cone 6.

FACTORS AFFECTING THE RESISTANCE OF SILICA REFACTORIES TO ABRASION.—F. A. Harvey and E. N. McGee (*J. Amer. Cer. Soc.*, **7**, 895, 1924). A simple apparatus for measuring resistance to abrasion is described. It resembles somewhat that employed in 1920 by Hartman and Kobler. An electric motor has a crystolon grinding wheel, 10″ by 1″, mounted directly on its shaft. Underneath this wheel is a carriage, moving on a track paralled to the face of the wheel. A force necessary to move the carriage is applied by the simple device of attaching a bucket to the carriage by means of a cord passing over a pulley. The bucket can then be weighted to apply a given pressure to the test piece. The wheel is allowed to grind a *surface* groove against this pressure for a specified time (2 minutes), whereupon the carriage is pushed back from the wheel and the length of the

groove made in the block is measured. This method gives large numerical differences for various refractories of the same class.

With the aid of the data obtained by this test, an attempt was made to correlate the factor of resistance to abrasion with other physical properties, such as porosity, apparent specific gravity, residual expansion, degree of burn, etc. The ability of a silica brick to resist abrasion does not appear to be dependent upon any one characteristic property of the brick, but it may be influenced by any one or more of the following properties : porosity, degree of burn, grind, quality of ganister, percentage of lime, physical structure or bond (workmanship). Other properties being approximately equal, the length of cut in a silica brick increases with porosity. The tabulated results showing the relationship between porosity and resistance to abrasion, range from 24·7% porosity, giving a cut 3·56 inches in length, to 29·7% porosity, showing 5·19 in. However, this relation is not absolute, particularly when bricks coming from different works or made from different types of quartzite are under consideration. No brick with a low porosity (24–25%) was ever found to be soft, but bricks having a porosity of 28–30%, or even higher, may be hard and give satisfactory service. No relationship was found between porosity or burn and modulus of rupture, but the length of the cut appeared to vary quite consistently with the degree of burn, as determined by the apparent specific gravity or residual expansion. The effect of re-firing silica bricks in the kiln was to increase their resistance by 20 to 30% and to decrease the porosity by about 3%. This higher resistance is probably due to the formation of a hard skin and a stronger bond rather than to a change in porosity. All the abrasion tests were carried out at ordinary temperatures, the assumption being made that approximately the same ratio would exist for working temperatures also.

CLASSIFICATION OF REFRACTORIES.—V. Bodin (*Cer.*, **28**, 1, 1925). A system of classification has been worked out, and applied to 34 qualities of bricks each of which had been treated for chemical composition, fusion temperature, refractoriness, percentage linear variation after firing for 3 hours at 1,400°C., 3 hours at 1,500°, and 2 hours at 1,600°, the temperature at which contraction took place and the crushing temperature under a load of 10 kg. per sq. cm., the cold crushing strength, the regularity of dimensions, and the percentage absorption of water. All the bricks were the ordinary French commercial qualities, of the silico-aluminous or aluminous type. In order to establish a definite order among the products tested, a number was assigned to each test brick for each of the above-mentioned tests, based on the scale 0 to 10 ; *e.g.*, for the fusion test, a material having a fusion temperature of 1,800° was represented by the figure 10, another fusing at 1,500° by 1, and A third, having a fusion temperature of 1,730° being the figure 7·9. Similar figures were calculated for all the other tests. Certain coefficients were then assigned to each test in accordance with their relative importance. The chemical composition received the coefficient 3, the fusion temperature 2, refractoriness 5, and so on. Finally, the figures obtained for each test were multiplied by the respective coefficients, the results added together and divided by the sum of the coefficients. In this way, a number was obtained for each product, based on the scale 0 to 10, which represented its absolute quality ; the highest figure obtained was 6·9, and the lowest 3·25.

EUROPEAN SILICA REFRACTORIES.—S. S. Cole (*J. Amer. Cer. Soc.*, **8**, 55, 1925). A comparison between English and Continental and American silica refractories is made. Five European ganisters (not named) were first analysed and made up into bricks by the ordinary American methods. Subsequent tests on these bricks showed that they were equal in quality for coke and gas oven construction to those made of American material. The bricks made from one of the ganisters, containing 98·0% SiO_2, 0·93 Al_2O_3, 0·54 Fe_2O_3, 0·07 each of CaO and MgO, trace of alkalies, and 0·29 loss on ignition, was particularly promising. The bricks and shapes manufactured in Europe were submitted to the usual tests. In general, the European ware was of

fair workmanship and quality, but the bricks were not well bonded, were underfired and low in fusion point. Some of the bricks gave conclusive evidence of being bonded with clay. A general tendency toward bricks of Dinas and quartzite quality was noted.

A GENERAL THEORY OF SPALLING.—F. H. Norton (*J. Amer. Cer. Soc.*, **8**, 29, 1925). It is suggested that it might be possible to determine the spalling qualities of a firebrick by measuring separately all the properties which affect spalling and then properly combining them into a single term. A theory is developed, according to which the spalling tendency (S) of a brick is proportional to the coefficient of expansion (Δ) divided by the square root of the diffusivity (h) and the maximum shearing strain (ϕ), thus $S = \frac{\Delta}{h\phi}$ Values for these properties were obtained experimentally on a number of bricks. Spalling tests, in which the bricks were heated to 1,593° and cooled in a current of air, were also carried out. The results were compared with the spalling formula by plotting the values obtained from the latter against the number of quenchings. The two were shown to agree satisfactorily on the whole. The fusibility of a brick can be varied greatly by suitable manufacturing methods. A small increase in flexibility greatly increases the resistance to spalling. The best non-spalling brick among those tested had the greatest flexibility. In general, the most flexible bricks are composed of rather large, hard grog particles held together by a soft porous bond.

ARTIFICIAL SILLIMANITE AS A REFRACTORY. I.—H. Wilson, C. E. Sims and F. W. Schroeder (*J. Amer. Cer. Soc.*, **7**, 842, 1924). Sillimanite has a high melting point, a definite chemical composition, and a crystalline structure. Crystalline materials have the property of resisting deformation at temperatures very close to their melting points. Crystalline sillimanite is a compound composed of three molecules of alumina and two of silica ($3Al_2O_3.2SiO_2$). An investigation has been conducted to study the refractory properties of electrically fused mixtures of silica and alumina, including fused quartz, fused fireclay, English china clay, and mixtures of china clay and alumina. If chilled suddenly from a temperature above 1,810°, mixtures containing more than about 55% alumina will contain corundum and glass, but if cooled slowly through the fluid zone they will contain 3 : 2 sillimanite and silica glass when the alumina content is from 55 to 71·7% ; and 3 : 2 sillimanite and corundum when the alumina is more than 71·7%. Sillimanite can be made by reducing the silica in clay by adding carbon to the charge. The silica removed is partially reduced to SiO, which is volatile at the temperature of reduction and escapes as a gas. The remainder of the silica is reduced to silicon, most of which forms metallic globules of ferrosilicon. The presence of ferrosilicon is troublesome, because it oxidises during the firing and ruptures the bricks. It can be removed by adding iron turnings to the charge. This not only increases the specific gravity of the ferrosilicon (FeSi+Fe), thus causing the globules to settle at the bottom, but, if enough iron is added, it is rendered magnetic and can then be separated easily. The tests carried out were : chemical and petrographic analyses, cone fusion, and high temperature under-load tests. After the removal of the ferrosilicon, the fused material was crushed to pass a 2-mesh sieve, and that portion which passed a 4-mesh was further reduced to pass a 20-mesh sieve. All magnetic ingredients were removed. These melts were made of an American fireclay and one of the best grades of English china clay. These melts had an alumina-silica ratio of about 68 to 32. The glass content, although small, was sufficiently active to prevent good resistance to load at high temperatures. When the alumina content was increased to 70%, corundum appeared as another crystalline phase. Mixtures containing from 71·7 to 100% alumina showed an interlocking structure of corundum and artificial sillimanite, with only traces of glass. Good results were obtained in the under-load tests with this type.

ARTIFICIAL SILLIMANITE AS A REFRACTORY. PART II.—H. Wilson, C. E. Sims, and F. W. Schroeder (*J. Amer. Cer. Soc.*, **7**, 907, 1924). The silica brick is the only one of the usual types of refractory which is capable of carrying a load such as that of the roof of the openhearth steel furnace for continuous service at temperatures above 1,500°. The lime-alumina-iron silicate flux is so well distributed in the silica brick structure and is so small in amount (6% maximum) that, on fusing, it cannot lubricate the adjoining grains, and thus cause failure, but can only form a liquid medium for solution, saturation, and recrystallisation of the silica. Thus, an interlocking crystalline structure is developed, which will resist loads at high temperatures very near to the melting point of the crystalline material. Refrax bricks, made by recrystallising silicon carbide bricks in the electric furnace, is another example of the crystalline bonded structure which will withstand loads at high temperatures. Both sillimanite and refrax bricks of crystalline bond will resist a load of 25 lb. per sq. in at higher temperatures than silica bricks. Resistance to slagging and to temperature changes are other doubtful points.

Sillimanite refractories were subjected to comparative tests with other types for thermal shock resistance, both by the water-quenching and the air-cooling spalling test method. The stony type of sillimanite was superior to the glassy type in both tests, and gave better results than commercial zirkite, silica and magnesia bricks. Refrax bricks developed a series of cracks which were distinctly visible when the bricks were red hot, but separate portions could not be removed by hand. Resistance to spalling was also tested by measuring the loss in compressive strength. The bricks were cut into halves, one half being crushed cold, the other heated to cone 14 (1,350°), and maintained at this temperature for one hour, after which it was cooled on edge in still air for an hour. The process was repeated twice. Both the silica and the magnesia bricks were total losses after one rapid heating. The refax bricks split into halves after two heatings, but each half retained 73% of the original strength. The sillimanite bricks gave the highest crushing strength (8,190 lb. per sq. in.), but retained only 59% of this after two heatings.

The refractories were tested for resistance to clog action both by the cone-fusion method and by the bath test. Slags with a high lime-content showed the greatest activity on all the refractories except chrome and magnesia. The silica was affected by slag appreciably less than the sillimanite samples. Furthermore, the lime-content was a very important factor with the sillimanite and the zirkite, but caused little difference with the silica. Under the bath test, a silica brick standing in a 4-inch bath of basic slag was entirely dissolved before the magnesia brick softened or spalled enough to give way, and before the base of the sillimanite-corundum brick had disintegrated. A general summary of the results obtained in the laboratory tests indicates that: (1) Sillimanite-corundum bricks withstand higher temperatures than silica, magnesia, chrome, firclay or zirconia bricks; (2) sillimanite corundum mixtures resist load at high temperatures better than any of the common refractories, except refrax, and better than sillimanite-glass bricks; (3) though hard and dense, they resist spalling better than silica and magnesia material, but they are inferior in this respect to fireclay. A more open structure may be developed to give greater resistance to spalling where resistance to load is not essential; (4) They resist acid slags; and the structure can be made sufficiently dense to give greater resistance to basic slag than that of open porous silica bricks; (5) lime in sillimanite as an impurity in excess of 1·5% seriously reduces the fusion temperature.

COMMON SENSE AND COMMON REFRACTORIES.—M. C. Booze (*Chem. Met. Eng.*, **31**, 1,003, 1924). The possible future developments in fireclay and silica refractories, and the practical limitations to which the quality of the product is confined, are discussed. The shorter life of refractories is not due to inferior ware, as compared with that formerly produced, but rather to increased demands made upon furnaces in general. The chief cause of failures is the increased working temperatures. Refractories made

of chrome, magnesite, silicon carbide, fused alumina are indispensable in certain branches of industry, but their use is limited and they are expensive. The major portion of all refractories used at the present time comprises those made from silica and from various combinations of silica and alumina, and it is to these that attention is devoted.

Fireclay refractories. Natural fireclays usually soften at a temperature about two cones (*i.e.*, 40°C.), lower than the theoretical temperature for corresponding mixtures of pure alumina and silica. This is due to the presence of such fluxes as Fe_2O_3, CaO, MgO, TiO_2, Na_2O and K_2O, present in the clays as pyrite, siderite, magnetite, magnesite, etc., They may be partially removed by weathering, by low temperature calcination, by leaching with acid, and by washing. Weathering or washing has little effect upon the flint clays however, since the lumps are not disintegrated by water. Furthermore, all these processes add to the cost of production considerably. From a 1 to 4 mixture of a plastic clay having a fusion point of cone 28-29 and a flint clay fusing at cone 33, a fireclay brick is produced which fuses at cone 32 (minimum). If plastic clay having a fusion point of cone 30-31 is used, the fusing temperature of the bricks is increased to cone 32-33, *i.e.*, about half a cone higher. Bauxite does not cease to shrink until it has become brittle and susceptible to spalling ; its use has been practically discontinued. Diaspore bricks have proved to be well suited to certain conditions. The raw material contains from 10 to 30% of silica, and the cost of mining it is considerable. New and cheap sources of high-grade materials such as diaspore, sillimanite, andalusite, etc., may possibly be discovered, but, for the present, fireclays will continue to furnish the bulk of refractories used, and no marked improvement in quality can be expected of products made from these.

Silica refractories. Silica refractories are replacing fireclay products in many continuous furnaces. The Medina, Baraboo, and Alabama quartzites, from which most of the American silica refractories are made, differ but slightly from each other in chemical composition. They contain about 97·5% SiO_2, 1·5–2% Al_2O_3 and Fe_2O_3, and 0·5% lime, magnesia and alkalis. The strength of the fired brick is determined largely by the grind, the amount of glass present, and by the crystal intergrowth. About 75 to 80% of the quartz is converted into cristobalite and tridymite, the amount of inversion being determined by the temperature and duration of the firing and by the action of the fluxes and the lime. The maximum silica content is between 98 and 99%. Maximum inversion during firing should be aimed at, in order to avoid undue expansion of the bricks in use. Tridymite changes from the alpha to the beta form less sharply, and with less volume change than is the case with quartz and cristobalite ; hence, bricks consisting largely of tridymite are less susceptible to spalling than bricks in which the other forms predominate. In the presence of a flux, quartz inverts slowly at 870° to tridymite, which, in turn, inverts to cristobalite at 1,470°. Without a flux, tridymite is not formed, the quartz going directly to cristobalite at 1,250C°. In a silica brick the fluxes are not sufficiently reactive to produce much tridymite ; the quartz changes to cristobalite, which then inverts slowly to tridymite on continued heating below 1,470°. After one fire at cone 15, an ordinary silica brick contained 26% quartz, 4% tridymite, and 70% cristobalite. After three firings it contained 16% quartz, 19% tridymite, and 65% cristobalite. At this rate, 10 firings would be required to produce 80% tridymite. To accomplish the same change in one firing, the kiln would have to be held for weeks at maximum temperature, causing much damage and consuming enormous quantities of fuel. Patents have been taken out covering the use of catalysts to increase the rate of tridymite formation, either in the brick itself or before the material is incorporated in the brick, but the results have not been encouraging. It is improbable that a refractory will be produced at moderate cost which is decidedly superior to those now on the market. Possible improvements may, however, be expected in greater uniformity in the raw materials used, in the structure and firing, and in the size and shape.

FIRECLAY BRICKS FOR THE OPEN HEARTH.—M. C. Booze (*J. Amer. Cer. Soc.*, **7**, 686, 1924). The use of fireclay brick for open hearth furnaces is confined almost entirely to the regenerators. In this position they are subjected to the heat of the outgoing gases, to the slagging action of the dust carried by the waste gases, and to temperature changes at frequent intervals. The waste gases enter the checker chamber at a temperature not exceeding 1,426°, but the bricks used must be of ample refractoriness to withstand extreme temperatures for short periods, due to abnormal operating conditions. The temperature change taking place when the draught is reversed is rapid, but covers a narrow range, so that spalling troubles are not serious. Owing to the manner in which the bricks are set, the load on the bottom bricks does not exceed 6 to 7 lb. per sq. in. ; furthermore, the temperature at the bottom is comparatively low, being about 370° to 530° below that at the top, so that little or no deformation or crushing occurs. This difference in temperature also accounts for the fact that the top checkers slag more readily and become eroded and clogged. When producer gas is used, it is considered that a run of 300 heats, without changing the checkers, is very satisfactory. Silica and magnesite bricks have been tried for the top courses, but without much success. Silica bricks were discarded because only a small percentage was recovered, owing to breakage. The temperatures in the gas checkers are lower than those in the air checkers ; hence the gas checkers are less subject to slagging. Since the waste gases entering the gas checkers go through a port below the centre of the passage to the air checkers, the dust carried into the former has a different composition to that entering the latter. This is shown by slag analyses.

THE EFFECT OF RED HEATS IN FIRECLAY BRICKS.—M. C. Booze (*J. Amer. Cer. Soc.*, **8**, 227, 1925). Bricks obtained from two different sources, some with typical red cores and others of the usual colour throughout, were subjected to various tests. The results indicated that, in general, the bricks with red cores were superior to normal bricks of the same composition, etc. The former proved stronger in the under-load test due to the strong bond formed by the iron while in the reduced state. This also showed less expansion in the reheating test and had a higher cold crushing strength. The spalling test brought out no appreciable difference between the cored and uncored samples after they had been subjected to the usual reheatings, but when tested without reheating some of the uncored specimens gave better results. The red cores were shown not to be due to a concentration of iron.

A NEW (ETCHING AND) STAINING PROCESS FOR TESTING REFRACTORY MATERIALS.—E. Steinhoff and F. Hartmann (*Stahl Eis.*, **45**, 337, 1925). The etching and staining process, well known in petrological practice, has been applied to the testing of refractories (*c.f.*, also A. Scott, *Trans. Geol. Soc., Glasgow*, **16**, 393, 1918). The etching solution consists of equal parts of conc. hydrochloric acid and saturated aluminium chloride solution. The gelatinised ingredients are stained by the action of a conc. solution of methylene blue. For the determination of structural ingredients containing lime, anthrapurpurine is used as the staining medium. In this case, the staining action does not represent an absorption process ; hence, etching is not essential. The success of the method depends upon the selective staining of the individual components. For instance, clay fired at or below 1,000° is stained a deep blue ; at 1,100° it is light blue ; at 1,200° almost colourless, and at 1,300° colourless. Unmodified quartz is colourless under the treatment, whilst modified quartz is stained sky blue. Differentiation was also effected between the various "contact zones," *e.g.*, clay-lime, clay-magnesia, clay-iron oxide, quartz-clay, and quartz-iron oxide. Both the clay-lime and the clay-magnesia contact zones are stained dark blue by methylene blue, but they are distinguishable when treated with anthrapurpurine, which gives a typical reddish-brown colour with ingredients containing lime. Examples of the practical application of the method are given. The complete test supplies data on the following : The firing temperature of fired clays and the amount of undesirable impurities present ;

the firing temperature of fireclay-grog bricks, the occurrence and distribution of quartz and localised lime and magnesia fusions, and the degree of modification of the quartz; the presence and position of thin layers of kaolin in quartzites, and the progress and type of the quartz modification; the extent of the quartz modification in silica bricks, and the behaviour of the silicate fusions.

TESTING FINE CERAMICS.—(*Rev. Mat. Constr. Trav. Pub.*, No. 184, 7 B, 1925). A review of the German methods of determining or calculating the physical properties, *e.g.*, true and apparent specific gravity, water absorption, tensile strength, bending stress, impact strength, etc.

NOTES ON REFRACTORY MATERIALS.—V. C. Faulkner (*Chem. Age*, **12**, 179, 1925). A high fusion point is not of paramount importance; thermal conductivity is equally important. The smaller the grain size, the better the thermal conductivity. Cementing materials should be reduced to a minimum. Refractory walls should be given two coats of refractory cement, so as to produce a glaze. British silica bricks are not burned at sufficiently high temperatures; they, therefore, expand too much on heating.

THE CHANGES WHICH TAKE PLACE IN SILICA BRICKS DURING THEIR USE IN OPEN-HEARTH FURNACES.—W. J. Rees (*J. Amer Cer. Soc.*, **8**, 40, 1925). At least four zones may be distinguished in the structure of a silica brick which has been in use in an acid open hearth furnace. The hot end consists mainly of cristobalite and magnetite and is more or less completely fused. The next zone shows traces of the original structure, but consists chiefly of tridymite crystals in a magnesite matrix. Ferruginous slag has penetrated both these zones. In the third zone a concentration of lime and alumina occurs; here, therefore, overheating may lead to fusion of the lining. The fourth zone is practically unaltered brick. Analyses and refractory tests are quoted to explain why the third zone rapidly fuses and drips when the first two have spalled away. For maximum durability of silica material, both high quartz conversion and high silica concentration are desirable. Greater structural stability of a furnace roof will indirectly promote durability in highly converted bricks.

V.—GLASS: GENERAL.

MAXOS: A JENA WATER-GAUGE GLASS.—H. Thiene (*Sprech.*, **58**, 45, 1925). The type of glass usually used for making water gauges is frequently attacked by the boiler water, a white opaque film being formed on the glass, so that, after a short time, it becomes difficult to read the water level. Figures are given, showing that Maxos glass is much more resistant to the action of pure water, and water containing 0·1% NaOH, and 0·5% Na_2CO_3, under pressure of 10, 20 and 30 at., than an ordinary type of glass.

SOME RECENT DEVELOPMENTS IN GLASS TECHNOLOGY.—W. E. S. Turner (*Industrial Chemist*, **1**, 32, 1925). A review of the progress made in the glass industry, both from a mechanical and chemical point of view, since the end of 1914 is given. Systematic investigations since 1917 in England have shown that replacement of silica by boric oxide has an important bearing upon the resistance of glass to water; maximum durability is attained with about 12% boric oxide. The results of a study of the changes occurring in the softening range are noted.

VARIATIONS IN GLASS CAUSED BY HEAT TREATMENT.—A. Q. Tool and C. G. Eichlin (*J. Amer. Cer. Soc.*, **8**, 1, 1925). Certain variations in the form of heating curves obtained with glass are due to changes in endothermic and exothermic effects, which vary in magnitude according to the nature of the previous heat treatment. These differences in the curves are relatively simple for many glasses, but somewhat more complicated for those having a high silica content. In the latter case the relationship between

these changes and the heat treatment is not so obvious. The previous heat treatment, is, however, always the chief determining factor. It is, therefore, suggested that a study of such curves would provide valuable information relative to the treatment of glasses. The density of glasses is also changed by varying the heat treatment, and it is indicated that other properties, including the solubility and resistance of chemical ware, may be controlled to some extent by similar means. The data obtained are utilised to explain the possible nature of the processes involved in the formation of glass.

A STUDY OF TANK FURNACE DEVELOPMENT.—H. L. Dixon (*Cer. Ind.*, **3**, 308, 1924). The flame should not impringe upon the glass, but should be 2. ft. above it. It is predicted that the electric furnace will come more and more into use. Individual furnaces, probably readily transportable, will be employed at each unit, and melting will be accomplished at a very high temp., so that much less time will be required than at present.

THE BASIC GLASS INDUSTRY.—A. Bigot (*Verre*, **4**, 243, 1924). A lucid account is given of the various types of basic glass, their composition, methods of preparation, etc.

THE THERMAL COEFFICIENT OF EXPANSION OF GLASSES AT HIGH TEMPERATURES, THE DEVELOPMENT OF STRESSES, AND THE ANNEALING PROCESS.—H. Schönborn (*Ker. Rund.*, **33**, 17, 1925). Apparatus is described by means of which the curves for thermal coefficient of expansion can be determined quickly and with sufficient precision for practical purposes. Heating and cooling curves for various types of glasses are discussed at some length.

COLLOIDS IN GLASS.—A. Silverman (*J. Amer. Cer. Soc.*, **7**, 795, 1924). The various elements and compounds present in a colloidal state in glass, *e.g.*, gold, selenium, chromic salts, platinum, etc., are discussed. The theory is not applied to copper-red glasses, this question being still unsettled. The action of X-rays and radium on soda and potash glasses, and the phenomenon of opalescence are also introduced in favour of the claim of the existence of colloidal suspensions in glass.

THERMAL EXPANSION OF FUSED QUARTZ.—G. E. Merritt (*J. Amer. Cer. Soc.*, **7**, 803, 1924). A sample of fused quartz reaches minimum length at—70°C., below which temperature expansion takes place down to—200°. Above—70° it expands gradually until at ordinary temperatures its expansion is ·5μ per meter per °C., which value it maintains up to 1,000°. The expansion curve from room temp. to 1,000° is almost straight. A maximum of 1·2μ per metre per °C. is reached at 1,100°. Curves are shown both for fused quartz and for several types of glass. A sketch is also given of the optical parts of the apparatus used in measuring thermal expansions.

Patents.

IMPROVEMENTS IN APPARATUS FOR DRAWING GLASS IN SHEETS.—C. Lanoy (*Engl. Pat.* 225,708, 10 Dec., 1923). In order to avoid the formation of longitudinal striations in sheet glass the distributing piece, or the lips thereof, is made of metals such as copper, nickel, gunmetal, nickel or copper alloy, to which the semi-fluid glass will not adhere, and which have a melting point higher than that of the glass. Iron, cast iron, or steel, which adhere uniformly to the glass may also be used. Brass must be water-cooled if used for this purpose, since its melting-point is below that of the glass.

IMPROVEMENTS IN PLATE GLASS ANNEALING LEHRS.—H. Wade (*Engl. Pat.* 225,789, 20 Nov., 1923). Addition to *Engl. Pat.* 208,014. The muffle chamber, in line with and communicating with a cooling lehr, has a number of heating flues, which extend longitudinally through the upper wall.

FURNACES FOR MELTING AND REFINING GLASS.—J. S. Shaw (*Engl. Pat.* 224,622, Aug. 23, 1923). A glass tank furnace is divided into a melting tank and a refining tank by a transverse bridge or wall, which projects a

suitable distance above the metal line of the furnace. The transverse wall has one or more dog holes or channels, connecting the two tanks together, and also two or more cold air and steam passages, arranged side by side and at right angles to the dog holes.

DELIVERING MOLTEN GLASS.—Hartford-Empire Co., Ass. of K. E. Peiler (*Engl. Pats.*, 227,078-9, 11 June, 1924). The forehearth is isolated completely from the tank above the level of the glass, and means are provided for communication between tank and forehearth below the level of the glass. The temperature and condition of the glass in the forehearth are controlled independently.

MANUFACTURE OF GLASS.—E. Zschimmer and P. Askenasy (*Germ. Pat.* 407,792, 5.12.22). A glass batch is compounded in such a manner that the finished product consists of at least one-third each of alumina and silica, not more than one-sixth of boric oxide, the remainder being barium oxide. The glass is suitable for making electrical insulators, being cheaper than porcelain.

COOLING AND ANNEALING SHEET GLASS.—H. Wade, Ass. of Empire Machine Co. (*Engl. Pat.*, 230, 261, 4/3/24). To equalize the temperature conditions above and below glass sheets when passing through the annealing lehr, the relative cooling effect of streams of gases, supplied to the tunnel both above and below the glass level at the charging end, is regulated by abstracting heat from the upper stream, by diverting a portion of the gases from one of the streams, by an arrangement of baffles, by adding heat to the lower stream, by increasing the natural velocity of the lower stream, or by a combination of these methods. The cross-sectional area of the lehr decreases from the changing end to the delivery end, whilst the floor slopes upward in the same direction.

ANNEALING FURNACE.—E. Chauncey (*U.S. Pat.* 1,525,644, 10 Feb., 1925. A fire box is situated over the lehr chamber and is connected with tunnel flues beneath the chamber by means of side-wall flues and transverse bottom flues. The tunnel flues communicate with the chimney. Means are provided for varying the draught conditions. The fire box above the chamber may be replaced by an inlet and an outlet chamber.

FUSED SILICA.—British Thomson-Houston Co. (*Engl. Pat.*, 228,191, 24/1/25). Crystalline quartz is heated until plastic, passed through a passage of gradually decreasing diameter to squeeze out the bubbles and cavities, and then allowed to congeal.

VI.—CEMENT, CONCRETE, MORTARS, ETC.

THE EFFECT OF THE SULPHIDE CONTENT UPON THE PROPERTIES OF BLAST FURNACE SLAGS AND CEMENTS.—R. Grün (*Stahl Eis.*, **45,** 344, 1925). The melting points and the microscopical and hydraulic properties of fused mixtures containing slags, both natural and synthetic, together with increasing proportions of calcium sulphide, were determined. A comparative series of tests, substituting calcium and magnesium oxides for calcium sulphide, was also carried out. The results showed that a fairly high sulphide content is not injurious to cements ; on the contrary, it increases the strength, and does not induce rapid setting, as is often assumed. When present in small quantity, the calcium sulphide forms a eutectic with the silicates, is taken up by them into solid solution at higher temperatures, and, on cooling, separates out in dendritic form. When present in large amount, it separates out in globular form.

SWEDISH SPECIFICATIONS FOR CEMENT.—(*Tonind. Ztg.*, **49,** 113, 1925).

THE BRITISH PORTLAND CEMENT INDUSTRY.—G. Martin (*Nature*, **115,** 150, 1925). A review of the book : "A Hundred Years of Portland Cement," by A. C. Davis.

MAGNESIA—PORTLAND CEMENT.—K. Balthasar (*Tonind. Ztg.*, **49**, 277, 1925). The part played by magnesia in Portland cement is explained. To produce a cement of good quality from materials containing considerable amounts of magnesia, the ordinary mixing and firing procedure must be modified considerably. The mixing must be based on a hydraulic modulus of 2·10, the hydraulic modulus being the ratio: $CaO/SiO_2+R_2O_3$. Four distinct stages are recognised in the burning process. In the final stage, the clinker must be held at sintering temp. for a considerable time.

HIGH EARLY-STRENGTH PORTLAND CEMENTS IN GERMANY.—G. Hayermann (*Eng. News-Record*, **93**, 910, 1924). Ordinary Portland cement occupies an intermediate position between the hydraulic limes, which exhibit slow but steadily increasing degrees of hardness, and the alumina cements, which reach maximum strength within a few days, subsequent increase being very slight. The tensile strength of high alumina cement or alcement, is low compared with the compressive strength. It is highly resistant to sea water and to water containing gypsum, but is less resistant to alkali sulphates. Acids and alcoholic liquids have a deteriorating effect upon alcements. The latter may not be mixed with the hydraulic cements, nor superimposed upon concrete of Portland cement, since this leads to disintegration. A further disadvantage of alcement is its present high price, which is 2½ times that of Portland cement. Present development is directed toward the production of high early strength Portland cements, having a strength and hardening properties not inferior to those of alcements at the early periods. The manufacture of these cements was not undertaken in Germany before 1924, in which year 17 works commenced operations. Strength tests on high-grade cement carried out by Ruth, proved that, according to the conditions of mixing and the amount of water applied, the safety point in loading beams was exceeded within 3 to 5 days. Other tests are described in which equally favourable results were obtained with regard to rapid hardening. In the manufacture of high-grade Portland cement, the same raw materials are used as for ordinary Portland cement. The composition is so selected that the cements have a high lime cementation index (0·99 according to the Newberry formula). Small quantities of iron ores, or calcined iron pyrites are often added to facilitate sintering and to increase volumetric stability. The composition should vary only to the extent of $\pm 1\%$. Finest pulverization and intimate admixture of the materials are of the highest importance. High early-strength cements are ground so that 2–6% remains on a 4900-mesh sieve, and 8–13% on a 10,000-mesh sieve. For ordinary American Portland cements a residue of 18–20% on a 200-mesh sieve is the usual practice. For fine-grinding purposes, preference is shown in Germany for compound mills made up of 2 to 3 chambers of considerable length, preferably several metres longer than at present, and equipped with air separators to remove the finest particles. In some cases, material of ordinary fineness is re-treated in a mill, in which the grinding media consist of steel sections, the size of a finger joint, and rivet punchings. The clinker must be well burned, but not smelted, and coal comparatively free from ash should be used. Firing with oil is highly recommended. From 3 to 4% gypsum, corresponding to 1·26–2·5% SO_3, should be added; this small quantity increases the strength. Gypsum causes disintegration only when added in excess of 5·5%. The initial temperature exercises a great influence upon the early strength; an interval of 5° lowers the strength by 10% after a two-day test.

Patents.

TOP DRESSING MATERIAL FOR HARD TENNIS COURTS AND THE LIKE.—W. H. Porritt (*Engl. Pat.*, 225,269, 24 Aug., 1923). A surface material consists of clay coloured green by substances containing chromium, preferably chromium sesquioxide. Staffordshire clays which burn to a pale grey or to a pale buff colour give good results. The colouring agent is intimately mixed with the pugged clay, the amount required varying from 5 to

10% of the weight of clay. The product may be applied to the courts in this condition, or it may be dried and either fired to 1,000–1,300°, or vitrified. In an alternative method the chromium compounds are produced indirectly in the clay, during or after drying or firing, by the addition of sodium or potassium dichromate to the pugged clay.

MANUFACTURE OF ARTIFICIAL FREESTONE.—S. A. Fournier (*Eng. Pat.*, 223,884, 16/19/24). Non-chalky stone waste is mixed with dry cement and then moistened with an aqueous solution of zinc fluosilicate, alum, and molten tallow, the mixture being moulded under pressure. Suitable proportions are 1,500 cu. dcm. of stone waste, 200–500 kg. of cement, 180 l. of a liquid consisting of 100 pts. of water, 5 pts. of zinc fluorsilicate, 3 pts. of alum, and 7 pts. of tallow.

ARTIFICIAL STONE.—Kaiser Wilhelm Institut für Eisenforschung and W. Hessel (*Pat. J.*, 1,857, 1924). No. 218,275, June 17, 1924. Boiler slag or ash, either free from fuel particles or not, is ground, moulded, and heated to sintering point. The degree of porosity and the nature of the surface is affected by intermittent variation of the firing temperature.

MANUFACTURE OF A HYDRAULIC BINDER FROM BLAST FURNACE SLAG.—H. Löscher (*Germ. Pat.*, 407,410, 6/4/22). Fluxes are mixed automatically with molten slag on its way to a melting furnace, wherein the mixture is heated to a liquid condition, just sufficient water being then added to produce dry granulation. A highly uniform product is thus obtained with great economy of heat.

POROUS CONCRETE AGGREGATE.—B. J. Fallon (*U.S. Pat.*, 1,528,759, 10/3/25, Appl. 30/0/19). A mass of clay is first fired under oxidising conditions. Steam is then passed through the bed of burning fuel into the kiln and the firing continued in the atmosphere thus produced.

POROUS CONCRETE.—V. Wikhula (*Engl. Pat.*, 221,742, 17 Mar., 1924). Cement, mortar, concrete, etc., are rendered porous by mixing with the other ingredients natural or artificial snow or ice particles or hailstones. The snow or ice particles may first be mixed with a quickly hardening hydraulic material before being added to the mixture.

MANUFACTURE OF BLAST-FURNACE CEMENT, IRON–PORTLAND CEMENT, ETC., USING A NATURAL CLINKER.—H. Müller (*Germ. Pat.*, 407,654, 30/6/21). Dry blast-furnace slag is ground at a high temperature with sintered limestone in place of Portland cement clinker. The lime need not be slaked.

VII.—CHEMICAL AND ANALYTICAL PROCESSES.

METHOD FOR THE ANALYSIS OF ALUMINOUS SILICATE REFRACTORIES.—E. P. Barrett and F. W. Schroeder (*J. Amer. Cer. Soc.*, **8**, 68, 1925). The finely ground (200-mesh) refractory material is fused for 20-30 minutes with sodium carbonate, taken up in water and dilute sulphuric acid, filtered, ignited and again fused in potassium bisulphate. Sulphuric acid is then added to the combined fusion products, and the whole is evaporated until copious furmes of SiO_3 are evolved. Calcium sulphate is carefully removed by boiling in water. After filtering, the silica residue is treated with HFl and a little H_2SO_3, evaporated and ignited. The silica is completely volatilised as silicon tetrafluoride. The non-volatile residue is fused with potassium bisulphate. The alumina is determined by a method essentially similar to that described by Blum, The combined precipitates of iron and aluminium hydroxides are carefully ignited to constant weight at a temperature of 1,150°. Iron and other constituents are determined by any of the well-known methods.

VIII.—HISTORICAL, EDUCATIONAL, INSTITUTIONS, ETC..

NOTES ON FAENZA PAINTERS OF MAJOLICA OF THE SECOND HALF OF THE XIX. CENTURY; ANGELO MARABINI IN PARTICULAR.—E. Alberghi (*Faenza*, **12**, 40, 1924).

PORCELAIN TRADE MARKS.—O. Arendt (*Ker. Rund.*, **33**, 36, 1925). Illustrations are given of old trade marks of various nationalities, together with a few more recent marks and monograms employed by German manufacturers of electrical porcelain.

LEAD GLAZE DANGERS.—(*Chem. Age*, **12**, 155, 1925; *Analyst*, **50**, 133, 1925). Investigations carried out by the Ministry of Health showed that the glaze of certain earthenware casseroles imported from the Continent contained excessive quantities of lead, which, under certain conditions, might be dissolved from the glaze during domestic usage.

A MAJOLICA PIECE IN "SEVERE" STYLE WITH INSCRIPTION IN HIGH GERMAN.—G. Ballardini (*Faenza*, **12**, 5, 1924). A full, illustrated description is given of a majolica plate in the Museum at Faenza.

AN ANCIENT ARCHITECTURAL DECORATION IN COLOURED MAJOLICA IN RIMINI.—G. Ballardini (*Faenza*, **12**, 11, 1924). An illustrated account is given of the Sigismund Castle in Rimini.

COMMERCIAL RELATIONS BETWEEN FAENZA AND BAVARIA IN THE XVI. CENTURY.—O. Montenovesi (*Faenza*, **12**, 29, 1924). The text of a document dated October 7th, 1520, relating to a blue colour for majolica ware is given. A facsimile of the parchment, which lies in the state archives in Rome, is reproduced.

COUNT ALISSANDRO BIANCOLI'S "MAJOLICA POEM" AND OTHER CERAMIC RECORDS OF FAENZA IN THE XVIII. CENTURY.—L. Z. Naldi (*Faenza*, **12**, 33, 1924).

Physical and Chemical Survey of the National Coal Resources

In pursuance of the policy of carrying out the work of the above survey with the help of local Committees, the Fuel Research Board have appointed a committee to deal with the physical and chemical survey of the coal seams in the North Staffordshire area.

The composition of the Committee is as follows :—

Representing the North Staffordshire Colliery Owners' Association.
Mr. J. Cocks.
Mr. J. Gregory.
Mr. G. P. Hyslop.
Mr. E. P. Turner.

Representing the North Staffordshire Institute of Mining Engineers.
Mr. S. Henshaw.

Representing the Geological Survey of Great Britain.
Mr. J. A. Howe.

Representing the Fuel Research Board.
Dr. C. H. Lander (*ex-officio*), Director of Fuel Research.
Mr. F. S. Sinnatt (*ex-officio*), Superintendent of the Physical and Chemical Survey of the National Coal Resources.

Publications Received.

CAMBRIDGE AUTOMATIC TEMPERATURE REGULATORS. LIST No. 150. (Cambridge Instrument Co., Ltd., Grosvenor Place, London, S.W.1).

This is a well-illustrated catalogue of 20 pages, giving useful data regarding the automatic control of temperature. The Cambridge Regulators are applied to a large number of technical processes, from the control of atmospheric conditions in public buildings, factories, etc., to the regulation of temperature in galvanizing baths, melting pots for metals, enamelling ovens, and other high-temperature work.

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE, 1925. (L. Hill, London, E.C. 4). Ed. by D. M. Newitt, Ph.D., etc., 260 pp.

The catalogue—a first edition—was compiled with the cooperation of leading British Manufacturers of heavy and fine chemicals, machinery, plant and equipment. It is designed to become a standard book of reference for chemical, consulting, and contracting engineers, works' managers and others. The field embraces not only the chemical industry proper, but also all productive processes carried out by men having chemical training, including the ceramic branches. The book represents a compilation, in condensed form, of the catalogues of manufacturers. It is much more than a Directory, since it furnishes informative catalogue data arranged in such a manner as to provide as much detail as possible. An "Index to Industrial Applications," in addition to the Indexes to Space Users and Commodities, adds considerably to the value of the publication.

Abstracts.

I.—RAW MATERIALS.

GENERAL.

THE SO-CALLED "PSEUDOMORPHOUS" QUARTZ OF TERTIARY GOLD-SILVER VEINS.—P. G. Morgan (*Econ. Geol.*, **20**, 203, 1925). Platy, lamellar, or tabular quartz, as found in many mineral bodies, is shown not to be pseudomorphous, as has been frequently assumed.

GRAPHITE DEPOSITS OF ASHLAND, ALABAMA.—J. S. Brown (*Econ. Geol.*, **20**, 208, 1925). A full discussion is given of the surface features, geological setting, subdivisions, structure, age, origin, etc.

BIBLIOGRAPHY AND ABSTRACTS ON THE UTILIZATION OF PEBBLY CLAYS FOR HEAVY CLAY PRODUCTS MANUFACTURE.—F. T. Heath (*Bull. Amer. Cer. Soc.*, **4**, 165, 1925). The bibliography is compiled almost exclusively from American literature.

RAW MATERIALS OF THE GLASS INDUSTRY. II. BORAX AND BORIC ACID.—J. B. Krak (*Glass Ind.*, **6**, 98, 1925).

RAW MATERIALS OF THE GLASS INDUSTRY. III. SALT CAKE AND SODA ASH. I.—J. B. Krak (*Glass Ind.*, **6**, 123, 1925).

PROSPECTING FOR MINERAL WEALTH BY THE AID OF ELECTRIC RAYS OR WAVES.—(*Tonind. Ztg.*, **49**, 658, 1925). The old divining rod has now been superceded by apparatus, designed by Pastor, of Leipzig, and called the "Radio Emanator," by the aid of which the presence of any material, whether clay, china clay, coal, water, ores, or other minerals, can be detected at a distance of 30 km. Not only the presence, but also the thickness and extent of deposits, and even the depth and the nature of the overburden are indicated. On being bombarded with cathode rays, each element emits Röntgen rays of characteristic frequency. These rays can be made to react on a photographic plate (as in medicine), or be timed to given frequency (as in radio technique). By means of the Pastor apparatus, waves are emitted which are characteristic of the substance sought for, a sample of such substance (coal, clay, etc.), being placed in the apparatus. A resonance effect produced by these waves in the earth is proof of the presence of the desired material

RAW MATERIALS: OCCURRENCE, PREPARATION, ETC.

BORAX AND BORIC ACID.—R. Freitag (*Emaillew. Ind.*, **1**, 61, 1925). The methods of preparation from the different raw materials are described. In Germany, boric acid is prepared from the large Chilean and Californian deposits of sodium borocalcite solely by treatment with sulphuric acid: $2(CaB_4O_7+NaBO_2+6H_2O)+3H_2SO_4=2CaSO_4+Na_2SO_4+10H_3BO_3$.

MAGNESITE FOR FURNACE BRICKS.—(*Master Builder, Brick Suppl.*, No. 757, 61, 1925). A brief account is given of the principal deposits in Europe and N. America, and of the methods of preparation. Chemical analyses of four Italian magnesites are included.

AGE AND ORIGIN OF THE LOUGH NEAGH CLAYS.—W. B. Wright (*Quart. J. Geol. Soc.*, **80**, 468, 1924). The Lough Neagh clays are superposed on the Upper Basalt and separated from it by a deep zone of weathering. They are associated with the older Tertiary, and are not Pliocene. The source of the clay was the 70 feet of soft lithomarge capping the unaltered basalt. The clay contains 10·5% of titanium oxide, and has been used for some time for pottery purposes.

RAW MATERIALS.—THEIR PROPERTIES AND USES.—A. F. Greaves-Walker (*Cer. Ind.*, **4**, 447, 1925). The first of a series of articles dealing with the ceramic raw materials. Bentonite and andalusite are discussed.

RAW MATERIALS OF THE CERAMIC INDUSTRY—(*Chem. Met. Eng.*, **32**, 618, 1925). Recent investigations of the (Amer.) Bureau of Standards are described in general terms. Comparative tests on English and American clays showed that the former gave stronger bodies. Flint of different varieties was tested for firing behaviour, porosity, bulk sp. gr., etc. The affect of substituting American for French flint is noted. The effect of salts on clay suspensions has been studied with a view to obtaining physical-chemical constants for specification purposes. The problem of drying clays is also receiving attention.

SYNTHETIC SILLIMANITE IN CERAMIC BODIES.—T. S. Curtis (*J. Amer. Cer. Soc.*, **8**, 63, 1925). The manufacture, characteristics, and use of a new ceramic product, in which the stable form of silimanite ($3Al_2O_3.2SiO_2$) is the chief constituent, are described. Every known form of sillimanite—andalusite, cyanite, natural (Indian) sillimanite—and every possible artificial mixture was used, and in all cases heat treatment was found to change the mineral or mixture into a mass of crystals composed of 71·8 alumina and 28·2 silica, corresponding to the formula $3Al_2O_3.2SiO_2$. A composition was finally evolved which consisted of a readily fusible glass matrix, of definite and controllable composition, in which an abundance of 3 : 2 sillimanite crystals grew as the melt cooled. When used with a typical ceramic body mixture, the glass readily melts into the body, acting in a manner similar to felspar, and permitting sillimanite crystals to form anew. These crystals interlock and interlace, giving great strength and toughness to the product. It was found that slight traces of alkali persisted in the crushed product, owing to the reducing atmosphere under which it was formed. This alkali, which would act as a deflocculent in many bodies, is eliminated by suitable treatment, so that the addition of the finely ground material has the same effect on the working properties as so much felspar or flint. The new ceramic product is described as rich in pure sillimanite crystals, imprisoned in a matrix which permits a ready blending and solution with the ball clay and china clay of the bond at temperatures within commercial reach, acting like felspar in high temperature bodies, and combining with the felspar in low-fire compositions. The electrical properties of the product are good. Synthetic sillimanite has given good results when used as pebbles in ball mills ; the sillimanite pebble has a specific gravity of 3·1 (flint about 2·6).

RAPID CHECK-TESTING FOR FELSPAR FOR USE IN VITRIFIED FLOOR TILES.—N. A. Ragland (*J. Amer. Cer. Soc.*, **8**, 391, 1925). Fresh supplies of felspar are first carefully sampled, and the samples are then thoroughly dried at 100°. Trial bodies are then prepared, in which the felspar content is varied at the expense of the flint to the extent of 4% above and below that of the current works standard body, the clay content being maintained constant. Test pieces are prepared and fired in a uniform manner from these bodies and tested for shrinkage, porosity and correct firing. Test pieces are retained for purposes of comparison with succeeding supplies of felspar.

QUANTITATIVE DETERMINATION OF THE DEVELOPMENT OF MULLITE IN FIRED CLAYS BY AN X-RAY METHOD.—L. Navias (*J. Amer. Cer. Soc.*, **8**, 296, 1925). X-Ray patterns were obtained by the powder method for mullite, prepared in quantity by fusing silica and alumina in the correct proportions, and for a number of ball clays and an English china clay, fired either alone or with felspar as a flux. Comparison of the X-Ray patterns indicated that the crystalline development in the fired clays was similar to the crystalline compound mullite. Calculated as weight percentages of the raw clays, the amount of mullite developed in clays fired to cone 10 was 33, 33, 40 and 50% for the ball clays and 60% for the china clay. Each clay developed the maximum quantity of mullite theoretically

possible according to the chemical composition. Small variation only was detected between the clay substance of the china clay and that of the ball clay, the criterion being the development of mullite on firing.

II.—MANUFACTURING PROCESSES

GENERAL.

A NEW CERAMIC MATERIAL: "KERAMONIT."—(*Cer. Ind.*, **4**, 294, 1925). "Keramonit" is prepared by embodying a mesh or skeleton of suitable metallic composition, in a ceramic mass, the procedure resembling that followed in making wire glass. The product is fired at a high temperature which has the effect of welding the metal skeleton and the ceramic mass into a solid union. The finished body has a hard "ring," from which it is concluded that the union is not merely mechanical. Various metals are used, according to the special properties desired, *e.g.*, iron, nickel, chromium-nickel, and for the ceramic mass, certain clays or other fire-proof material. The material is immune from the effects of extremely rapid and violent changes of temperature; crucibles can be heated to any temperature and plunged into cold water without cracking. The mechanical strength is also remarkable; such a crucible may be dropped on a hard stone floor without damage. The material is also an excellent conductor of heat and a variable conductor of electricity. Hollow bodies can be made of "Keramonit" with walls as thin as 0·5 mm. In this thin form, the material is remarkably elastic; a strip can be wound into a spiral without loosening the ceramic mass, or can be bent over a sharp edge.

MANUFACTURE OF ARTIFICIAL TEETH.—Freymuth (*Ker. Rund.*, **32**, 706, 1924). The three raw materials, china-clay, felspar and quartz, are first coarsely ground in an edge runner, then mixed in predetermined quantities, (if necessary, with the addition of colouring matter), and ground very finely in porcelain or earthenware ball mills. The colloidally fine powder is then made up into a plastic mass and moulded in suitable moulds into the desired shapes (incisors, molars, crowns, etc.). The pin may be either soldered or fired in the porcelain tooth. In the first case, a small platinum collar is embedded in the unfired tooth, whilst in the second case the platinum or gold-platinum alloy pin is introduced directly into the tooth. The teeth are then fired in gas or electric furnaces to a temperature of 1,500°C. The fired teeth are subjected to various tests before being passed out. For hardness they are tested in a sclerometer, consisting of a weight sliding on two graduated vertical guide rods. Transparency is tested in a diaphanometer, which, though less accurate than the selenium cell, is more easily handled and gives quicker results. To test the density and homogeneity, a tooth is ground away on two sides and immersed in a colouring solution. The fact that the soldering operation is carried out with an open flame is taken as a guarantee that the teeth are resistant to high temperatures. The rigidity of the pin is tested in a special apparatus. Each pin is gripped between fine forceps, tension being applied in a horizontal direction. Another machine serves to apply a leverage test which aims at simulating the pressure conditions corresponding to the act of chewing. Sample teeth are taken at random from the daily production and vulcanised into strips of rubber, which can be set at any angle in the machine, so that it is possible to adjust the test so as to reproduce an nearly as possible the usage to which the teeth are exposed in the mouth. The platinum-iridium pin has been abandoned, owing to its high price, in favour of the sixty-forty gold-platinum alloy, or of the gold-plated pin with nickel core. The former is fired directly in the tooth, whilst the latter is soldered on to a platinum collar which has previously been fired in. The gold-platinum alloy is equal in every respect to platinum for dental purposes. A free zone is provided around part of the pin embedded in the tooth, this zone being filled with solder or rubber. The gold-platinum and gold-plated nickel pins are proof against any chemicals of a basic or acid nature which may be present in the

mouth, but, on the other hand, they may be exposed to the electro-chemical action of electrolytes present in the saliva, such as alkaline chlorides, calcium phosphate, potassium thiocyanate, formed by biochemical process in the body itself. In the manufacture of the pins for porcelain teeth, metals are chosen with the lowest electrolytic solution pressure (silver 10^{-15}, gold 10^{-25}, platinum 10^{-30} Atm). Thus there is little danger of serious deterioration during the lifetime of the individual.

MANUFACTURE OF HIGH-VOLTAGE INSULATORS.—Hunt (*Chem. Met. Eng.*, **31**, 731, 1924). The raw materials used in making high tension insulators are, mainly, ball-clay, kaolin, felspar, and silica, together with small amounts of fluxes if necessary. Curves are reproduced, showing that both the dielectric strength and the resistance to impact are increased by regrinding, for four hours, commercial flint and felspar. The small amount of organic material, which is always present in ball clays, has to be eliminated, but the quantity present is too small to justify a separate washing operation. After the ball-mill charge has been transferred to the mixing tank, the mixture, suspended in water, is run through a series of screens, graded from coarse to extremely fine, to eliminate all dirt. It is then passed over a large magnetic separator, and is finally stored in large cisterns beneath the floor. After being filter-pressed, the plastic body is passed through a special mill, which converts the filter cakes into a reasonably homogeneous mass, which is aged in cellars for several weeks. The insulators are formed almost exclusively by the hot-pressing method. A hot, revolving metal tool is forced into a mass of plastic clay, contained in a plaster mould, the tool forming one surface of the insulator and the mould the other. Small insulators are made in a small press, whilst a large, massive press, the largest used for this type of work, turns out the largest size at the rate of several hundreds per hour.

Drying is done in two stages, first a preliminary drying in the mould followed by a final drying after the unit has been trimmed and smoothed. The glaze is applied by dipping or by spraying, usually by the former method. The glaze is generally a natural clay, to which manganese dioxide, red iron oxide and chromium oxides are frequently added in small amounts. The insulators are fired in saggars for a period of about 68 hours, the fuel used being gas for the early, low temperature stage, and fuel oil for the final stage. The finished insulator is subjected to a severe test. The electrical test consists of applying a sufficiently high voltage to cause arcing over its surface, this arc being maintained for from 15 to 10 minutes. The voltage required depends upon the shape of the unit. Test losses in modern insulator works should not exceed 2 per cent.

THE PRESENT POSITION IN THE MANUFACTURE OF PORCELAIN INSULATORS IN AMERICA.—B. Schapira (*Ker. Rund.*, **33**, 33, 1925). An article compiled from American literature, published between 1913 and 1923.

AMERICAN PAVING BRICKS.—J. B. Monnier (*Cer.*, **28**, 28, 1925). A short review, from American literature, of the method of manufacture, properties, uses, advantages, etc., of paving bricks.

BRICKMAKING AND USE OF BRICKS IN SWEDEN. II.—G. W. Cronquist (*Claywr.*, **83**, 530, 1925). Continuous kilns are used almost exclusively. One or two drying floors are built over the kilns.

FLOOR TILES.—E. Tuschhoff (*Ker. Rund.*, **33**, 169, 1925). A general account is given of the manufacturing process and of its development.

Patents.

CEMENTING INSULATORS.—Porcelainfabriken Norden Aktieselskabet (*Engl. Pat.*, 230,445, 2/3/25). A slip made from the insulator material and grog of the same nature is applied, before firing, to the surfaces of parts of insulators to be joined together, or to metal. The parts are then fired.

JOINING INSULATOR PARTS.—Porcelainfabriken Norden Akt. (*Engl. Pat.* 230,446, 2/3/25). The upper, bell-shaped portion of an electric insulator is connected to the lower stem member by a coupling member, adapted to transmit tensile stress.

EARTHENWARE.—H. Oexmann (*Engl. Pat.*, 231,469, 14/3/25). The clay, or body mixture, is subjected to high pressure (300 atm,), the process being applied either to the mass or to shaped articles. The pressed article may be turned, and is then fired. Pressure may be applied through a gaseous, liquid or powdered medium.

REFRACTORIES CONTAINING RUTILE.—A. L. Mond, for Metal and Thermit Corporation (*Engl. Pat.*, 232,679, 23/1/24). Articles are formed from ground titanium dioxide either by pressure simply, or with added water to form a paste, or with 1–2% of a binder such as clay, alumina, sodium silicate, bentonite, etc., and then fired to above 800° to agglomerate the rutile. Other refractory substances such as zirkite may also be added.

TITANIUM DIOXIDE AS A REFRACTORY.—A. L. Mond, for Metal and Thermit Corp. (*Engl. Pat.*, 232,680, 23/1/24). A black form of titanium dioxide, which is a conductor of heat and electricity, is obtained by heating rutile to a temp. well below fusion point (800-1,000°) in a reducing or neutral atmosphere.

COMPOUNDING AND PREPARATION OF BODIES, ETC.

FINE STONEWARE FROM FLINT CLAY.—P. E. Cox (*J. Amer. Cer. Soc.*, **8**, 257, 1925). A stoneware body, containing 60% of flint clay, 19% of ball clay, 14% of felspar, and 7% of bentonite, proved suitable for the manufacture of art stoneware, ball mill fittings, mosaic floor tiles, and certain types of electrical insulators. The body has excellent "working" properties, and can readily be glazed. The flint clay used contained about 44% of silica and 40% of alumina, its deformation point being cone 34.

ZIRCON AS A CONSTITUENT OF CERAMIC BODIES.—W. L. Shearer (*Ceramist*, **5**, 316, 1925). Zircon consists, chemically, of one molecule each of the earth zirconia and silica, the formula being: $ZrO_2.SiO_2$ or $ZrSiO_4$. When pure, it contains 67·2% ZrO_2 and 32·8% SiO_2. Zirconium occurs in deposits not only of the silicate, but also of the oxide, baddeleyite, as, for instance, in Saõ Paulo, Brazil. Zircon is a very stable, well-crystallised mineral having extraordinary hardness, high density, and a high thermal expansion coefficient. Experiments were carried out with zircon obtained from beach sands in Florida which, after purification, consisted of 98·5 zircon and 1·5% impurities (Al_2O_3, TiO_2, Fe_2O_3, and P_2O_5). For resistance to thermal shock, the following bodies were developed :—

	No. 8.	No. 19.	No. 30.
Zircon	30%	60%	75%
Whiteway Engl. ball clay ..	15	10	20
A1 Eng. china clay	22	—	—
Edgar Plastic kaolin	10	—	—
Flint	3	—	—
Talc	20	3%	—
Atlas ball clay	—	7	—
S.C. kaolin	—	8	—
$MgCO_3$ ppd.	—	1	—
Felspar	—	11	—
Rutile	—	—	5

The properties of these bodies, when fired to cone 12, were as follows :—

	No. 8.	No. 19.	No. 30.
Percent porosity	20·2	11·6	21·0
Percent absorption	8·9	4·1	7·0
Bulk sp. gr.	2·28	2·86	3·01
Transverse strength, lb./sq. in. ..	6200	9500	7600
Strength after quenching ,, ..	2400	3500	2500
Dry transverse strength ,, ..	290	400	350

A high porosity was maintained in order to give greater resistance to temperature changes. The method adopted in the quenching test was unusually severe. Test bars, at room temperature, were suddenly placed in an electric furnace heated to 950°C. After the bars had been heated uniformly to this temperature, they were withdrawn suddenly and cooled as rapidly as possible in a current of air from an electric fan. This treatment was repeated three times, after which, if the bars remained apparently intact, they were tested again for transverse strength. The decrease in strength is given in the above table. Under this treatment, an ordinary porcelain would fly to pieces on the first heating.

Certain hard porcelain for special purposes were also developed, as, for instance :—

High Fire Porcelain.		*Grinding Pebbles.*	
Zircon	40%	Zircon	52%
Whiteway Engl. ball clay ..	5	Wh. Engl. ball clay ..	15
A1 Engl. china clay	20	S.C. kaolin	8
Florida kaolin	10	Felspar	25
S.C. kaolin	5		
Calcine No. 1 *	20		

Properties (Cone 17).		Properties (Cone 12).
Porosity	0·3%	6·0%
Absorption	0·1%	2·2%
Bulk sp. gr.	2·91	2·88
Trans. str. lb. sq. in. ..	10,000	8500
do. after quenching ..	3500	3300
	(Slight tendency to dunt)	(Will dunt)
Dry trans. str.	240	370

* Magnesium carbonate 24·6, kaolin 75·4, approx., composition $MgO.\ Al_2O_3.\ 2SiO_2$ (Cone 12).

The working properties of these bodies are very good. The tendency to dunt on quenching could be largely overcome by suitable changes in the clays and fluxes used. A characteristic property of zircon is to impart high mechanical strength to a body; talc has the opposite effect. Grinding pebbles or ball mill linings, made from the above body, would not only outlast flint pebbles, but would grind more efficiently, owing to their greater weight. The sp. gr. of most body ingredients is about 2·6, whilst that of zircon is 4·7. In a casting body there is naturally a slight tendency for the zircon to settle out; yet zircon bodies can be cast successfully if the slip is properly prepared. Good crucibles have been cast in the ordinary way, without cores, with a body containing 10% English ball clay and 90% zircon. The weight of water amounted only to about 20% of the dry weight of the body, 0·05% soda ash and 0·07% sodium silicate acting as deflocculating agents. The sp. gr. of the slip slightly exceeded 3·0, corresponding to about 51 ozs. per pint. Another casting body was as follows: 70% zircon, 30% English ball clay, 28% water, 0·10% soda ash, and 0·09% sodium silicate, the weight of the slip being 38 oz. per pint.

BETTER TERRA COTTA SLABS.—F. B. Allen (*J. Amer. Cer. Soc.*, **8**, 101, 1925). The properties of good terra cotta slabs are: (1) High Refrac-

toriness, though this is not essential. It is controlled by the clay bond and by the grog ; (2) Mechanical Strength. This is very important, chiefly to ensure safe handling of the slabs in setting and drawing the kiln. It is a question of bonding clays and size of grog ; (3) Accurate Dimensions are desirable to facilitate rapid placing ; (4) Temperature Change. Resistance to sudden changes of temperature is an advantage, although under normal conditions such changes are slow ; (5) Spalling. Open firing clays show less tendency to spall because of their greater surface of radiation; (6) Abrasion. The slabs should be sufficiently tough to resist the rubbing action which takes place in setting and drawing a kiln ; (7) Thermal Conductivity. This should be relatively high in order to give an even distribution of heat. Slabs were made as the result of experiment, from the following mixture, produced on the volume basis, tempered by the ring method, and moulded by hand, sufficient water being added to render the mud "soft" : 30 grog, 15 clay of low plasticity, and 55 bond clays. The slabs appeared to possess the above characteristics.

A STUDY OF SLIPS FOR STANDARD FINISH TERRA COTTA (CONES 4–5).—H. E. Davies and J. S. Lathrop (*J. Amer. Cer. Soc.*, **8**, 23, 1925). The objects of the work were: (1) to ascertain the proportional limits of Cornwall stone, felspar, flint and clays in terra cotta slips at cone 4-5 ; (2) to develop a slip which would be highly vitreous, white, have a firing range unaffected by normal kiln variations, and, lastly, be free from crazing, checking peeling and flaking. The results obtained are illustrated by means of the usual triangular diagrams. They are summarised as follows: (1) A low clay content causes crazing ; (2) Good vitreous slips contained between 30 and 50% of clay ; too much clay decreased vitrification ; (3) The content of Cornwall stone should not exceed 50% ; more causes crazing ; (4) Good slips may contain felspar up to and possibly exceeding—35% ; (5) Flint increases the refractoriness, and tends to produce crazing; (6) Whiting decreases the firing range and acts as a refractory up to 5%; (7) Soda ash, added in the usual amount, has no apparent fluxing action. No combination of slip was found which would give a vitreous, and at the same time, a pure white product. Similarly, crow's-footing could not be eliminated entirely, but it is suggested that different methods of spraying, or the use of mica, might overcome this difficulty. The safe limits of composition for a vitreous terra cotta body at cones 4–5 are given as follows : Cornwall stone 25–30% ; felspar 0 to 35% ; clay 25–55% ; flint 0–10%.

NOTES ON TERRA COTTA BODY SHRINKAGE.—P. G. Larkin and E. R. Curry (*J. Amer. Cer. Soc.*, **8**, 113, 1925). In a new method of compounding terra cotta bodies, the materials are ground separately to pass a 14-mesh sieve and subsequently proportioned by disc feeders. When this method is applied in works practice, control shrinkage tests may be carried out in the laboratory. This was not possible under the old system. A variation of from 24·5 to 27·0% in the water content of a body increased the total shrinkage from 5·82 to 6·66%, the firing temperature being cone 4. An accurate method of controlling the water content would simplify shrinkage problems considerable.

MICROSCOPICAL OBSERVATIONS DURING THE PREPARATION OF BODIES AND GLAZES.—A Schoblik (*Ker. Rund.*, **33**, 430, 1925). By the use of the staining method (with aniline dyes), the microscope can be used effectively in the examination of bodies or glazes, to detect faults due to impurities or to insufficient grinding of the ingredients, and to distinguish such defects from those of smoking, etc. Examples are given, and illustrated, of faults due to calcite, dolomite, coarsely ground grog particles, felspar, and quartz.

DEVELOPMENT OF A CASTING BODY FOR VITRIFIED SANITARY WARE FROM AMERICAN MATERIALS.—A. Foltz (*J. Amer. Cer. Soc.*, **8**, 383, 1925). Comparative tests were conducted upon a number of English

and American clays by making up batches containing 50% clay, 25% felspar, and 25% flint. On the basis of the casting data obtained fron the individual clays, several casting bodies were compounded solely from American materials. A body was finally developed which cast up well in 2 hours and was satisfactory in other respects.

PATENTS.

MANUFACTURE OF CASTING COMPOUNDS CONTAINING SULPHUR.—E. Mandowsky (*Engl. Pat.*, 217,570, 22/5/24). Eleven parts (by volume), of sulphur are mixed with 8 parts of worked up spent purifying materials containing ferric hydroxide from gas works, colouring matter being added if desired. The mixture is then liquefied in containers and moulded.

POTTERY.—W. Vershofen (*Engl. Pat.*, 228,233, 24/10/23). Ceramic ware may be produced by partially converting the clay into a cement by the addition of calcium carbonate, soluble fluorides being usually added to start the chemical action. Silica is first added to clays which react weakly with fluorides. The moulded articles are first air-dried and then fired to a temperature below 1,000°. Suitable proportions may be 30% alumina, 5% sodium fluoride, 60% quartz, and about 5% calcium carbonate. Higher percentages of fluoride produce a non-separable glazed surface ; calcium salts prevent complete vitrification of the ware, which fires white and free from iron spots.

SHAPING, MOULDING, DRYING, ETC.

THE UTILISATION OF CASTING SCRAP IN THE CASTING SLIP.—E. A. Slagle and A. Foltz (*Ceramist*, **5**, 140, 1924). If scrap, which has been in contact with an absorbent mould, is returned to the blunger without having been thoroughly dried, it retains an indefinite quantity of the salts originally added to it. The slip is then seriously affected. If, however, the p_H (hydrogen ion concentration value of the scrap is determined and controlled, no difficulty arises in utilising the scrap. Casting slip is slightly alkaline and is usually somewhere between p_H 7·5 and p_H 8·5. Though this difference is extremely slight, it is of great importance. Experience has shown that the original p_H value of a clay has to be modified in order to produce a good casting slip. Plasticity is dependent to a great extent upon the degree of acidity, or the p_H value. The alkalinity, *i.e.*, the number of hydroxyl ions, is increased by adding such substances as soda ash, sodium silicate, sodium hydroids, etc., which act as deflocculators, causing the clay particles to become negatively charged. The addition of only 0·05% of a salt may be sufficient to ruin a slip for casting purposes. The optimum p_H value of casting slips has been measured, and methods have been devised for controlling this value when clay scrap is used. The figures at different plants varied from 7·4 to 8·6. Slight variation from these values caused casting trouble ; not only the raw materials purchased, but also the water may vary from time to time in p_H value. The test for determining the optimum p_H value is a simple one, and can be carried out in a few minutes.

FUNDAMENTALS UNDERLYING EVERYDAY DRYING OF CERAMICS.—A. E. Stacey, Jnr. (*Ceramist*, **5**, 6, 1924). The drying rate varies directly with the wet bulb depression and with the velocity of the air over the surface. The pieces should be arranged in relation to the drying surfaces. In the drying schedule, allowances should be made for a conditioning period for heating the material without loss of moisture, and a drying period. The former should consist of two parts ; in the first a relatively high humidity should be maintained during the time of shrinkage, and in the second the relative humidity should rapidly decrease.

EFFLORESCENCE ON POTTERY.—(*Ind. Eng. Chem. News Ed.* **3**, No. 9, 1925). To prevent injurious and undesirable efflorescence on pottery, the fresh moulds are coated with glue size, which burns off in the kiln. Since glue readily becomes putrid, preservatives are added in order to prevent the formation of

fungous growths during the drying process. This has not proved entirely successful, and it has been found advisable to give the size a resinous character. For this purpose, a synthetic resin is used which is made by heating a mixture of formaldehyde and phenol in the presence of alkali or other condensation catalyst. This synthetic resinous mass is added to the glue mixture in either thick or thin consistency. By this new procedure, no only are fungous growths prevented, but at the same time the ware receives a glossy surface which is harder than that previously obtained and is much more resistant to the action of heat and smoke fumes in the oven.

CASTING CONTROL.—A. C. Gerber (*J. Amer. Cer. Soc.*, **8**, 18, 1925). Correct proportioning of the clay is the most important factor in the preparation of a casting body. Ball clay is added solely to impart the necessary fluidity, whilst china clay is introduced to counteract the tendency to produce sections of uneven density. A simple test is described for determining the casting behaviour of clays. The use of electrolytes and of grog has a considerable effect upon the casting properties, but the chief factors are a balanced clay content and a correct ratio of clay content to non-plastic ingredients.

DYNAMIC SYMMETRY AS APPLIED TO POTTERY.—G. M. A. Richter (*J. Amer. Cer. Soc.*, **8**, 131, 1925). The fundamental principles are outlined, including a mathematical explanation, and an analysis of Greek vases is given.

Patents.

MOULDS FOR ARTIFICIAL TEETH, ETC.—Keradenta Porzellan-und Dental-Werke A. G. and K. Kammer (*Engl. Pat.*, 226,219, 12 Dec., 1924). Moulds are produced by taking negatives from an undivided pattern connected to a thin metal plate along the mould joint.

MOULDING CRUCIBLES.—C. T. Porter (*Engl. Pat.*, 231,470, 16/3/25). A punch is inserted to compress the material contained in a mould and a relative rotation of the punch and mould is effected while the material is undergoing compression.

KILNS, OVENS, MUFFLES; FIRING TECHNIQUE, ETC.

GAS-FIRED KILNS IN THE CERAMIC INDUSTRY.—N. Lengersdorff (*Sprech.*, **58**, 147, 1925). Descriptions are given of kilns of the Lengersdorff type suitable for firing ordinary bricks with damp lignite, or for the better types of bricks, refractories, earthenware, and porcelain with generator gas under pressure, using lignite briquettes as fuel.

GLASS FURNACES FIRED WITH POWDERED COAL.—O. Maetz (*Sprech.*, **58**, 151, 1925).

TESTING COAL IN CERAMIC WORKS.—E. Buss (*Sprech.*, **58**, 156, 1925). An account is given of the usual method applied, and the apparatus required, for determining the amount of ash and of hygroscopical and chemically combined water in coal, and its calorific value.

THE TUNNEL KILN.—(*Cer. Ind.*, **4**, 38, 1925 ; *Brick*, **66**, 22, 1925). The historical development of the tunnel kiln is sketched briefly and its advantages and disadvantages are pointed out. The twin tunnel kiln, which is rapidly coming into favour, can be built at lower cost than periodic kilns of the same capacity. As a rule, the water-smoking and preheating are done in one tunnel and the firing and cooling in the other. The first successful tunnel kiln in America was of the *Didier-March* type. Two fire grates are located on either side of the tunnel about midway between charging and discharging ends. The combustion chamber is separated from the main tunnel by an inner wall and the products of combustion pass through tuyères into the main tunnel. The waste gases and steam pass out into the chimney near the charging end, whilst the air for combustion enters through ports at the discharge end. Altogether about seven Didier-March kilns were built.

In the United States the *Dressler* kiln leads the way in having most installations of any one make. For many years efforts were confined by this organisation to kilns of the muffle type, in which the combustion chambers consisted of two lateral tubes of almost triangular section, running on either side of the tunnel toward its mouth. Recently, an open-fire kiln has been developed in which the draught is made to pass transversely across the tunnel, first from one side and then the other (see p. 7). The *Harrop* kiln is direct fired and is provided with furnaces on both sides in staggered relation. To prevent the top becoming hotter than the bottom, battered lining walls are used, which give increased space for horizontal gas movement at the bottom. The *Russell* kiln is also direct fired. Conditions in the preheating zone are controlled by dampers and side wall flues between the fire boxes and the exhaust fan at the entrance end. The cooling end is provided with hollow side walls and a hollow arch. The trucks have insulated refractory decks. The *Holcroft-Lengersdorff* kiln, developed in Germany, has recently been introduced into America. It has been used in Germany for firing various types of ware, from high-tension insulators to common bricks. It differs from other types mainly in the principle of heat application and heat recovery. A variable arrangement has been devised for the location of the burners in the high temperature zone, for carrying off the exhaust gases in the preheating zone, and for the recovery of heat directly or indirectly from the cooling zone. The charging end of the tunnel is practically converted into a separate compartment for drying and water-smoking. The various zones—drying, preheating, firing, and cooling—are not necessarily of fixed length, as is usually the case in tunnel kilns. The *Booth* kiln has proved very successful in firing face bricks. It is an open fire kiln, and has six fire boxes on each side. Coal is used for fuel. The second Booth kiln to be constructed is 335 ft. long, and has a bag wall to protect the ware from the flames. The products of combustion enter the kiln through small openings in the bag wall opposite the fire boxes a little above the level of the tops of the trucks. One fire box is left open entirely for the purpose of "flashing" the bricks. This kiln also has a hollow crown, in which air is preheated for drying purposes. Other successful kilns are the *Farber* kiln at the Farber Firebrick Co.'s plant, the *Marlow* kiln, the kiln recently installed by the Vitrefrax Co., of Los Angeles for firing refractories, and the kiln of small cross-section for firing sparking plug cores at the A. C. Spark Plug Co. The use of tunnel kilns has been extended much more widely to the porcelain and whiteware industry than to the heavy clay products branch. This may be due to the high initial cost. It is usually found necessary to make certain adjustments to tunnel kilns after the first fire in order to meet the requirements of the particular ware, since it is difficult to forecast exactly how any given clay will act in a tunnel kiln. This does not apply in the same degree to fine ceramic products. The following data were obtained from users of tunnel kilns in reply to a questionnaire: *Fuel Saving.* Tile making 79·43%; sanitary ware 56%; tableware 66·37%; refractories 53%; roofing tiles 63·75 and 60%; face bricks 45·7%; face bricks and firebricks 70%, and common bricks and tiles 75%; average, 63·28%. In many cases also the time taken in firing has been reduced by as much as 50%. *Labour Saving.* Sanitary ware 25%, 60%, 50% and 30%; stoneware 25%; tableware nil; refractories 40%; roofing tiles nil; face bricks 15%; face bricks and firebricks 40%; average, 28·50%.

AN ELECTRIC FURNACE FOR SOFTENING POINT DETERMINATIONS.—W. L. Pendergast (*J. Amer. Cer. Soc.*, **8**, 319, 1925). The furnace is of the Hirsch type, modified to the extent of the addition of a carborundum ring enclosing the hottest zone of the furnace, the object of the ring being to protect the fireclay shell at this point. The furnace which has been developed to meet industrial requirements is so designed that all parts can easily be replaced.

ADVANTAGES AND DISADVANTAGES OF THE TUNNEL KILN.—

(*Claywr.*, **83,** 526, 1925). Translation of an article appearing in *Tonind. Ztg.*, A report is given of experiences with Saarau tunnel kilns.

DESIGNING BANDS FOR ROUND KILN CROWNS.—B. W. Willson (*J. Amer. Cer. Soc.*, **8,** 154, 1925). The purpose of the paper is to analyse stresses in, and thrusts caused by a round kiln crown, and to select bands to withstand these stresses.

FIRING EARTHENWARE IN MUFFLE KILNS.—A. Schoblik (*Ker. Rund.*, **33,** 85, 1925). On-glaze colours, transfers, etc., on earthenware are fired on in muffle kilns to a temperature of about 800°. Certain practical difficulties encountered in this operation are discussed.

FIRING HOFFMAN KILNS WITH POWDERED COAL.—E. Spindler (*Ker. Rund.*, **33,** 134, 1925). The first section is devoted to the general problem of firing with powdered fuel, its advantages over grate firing being pointed out. A second section deals with the application of the method to the ceramic industry, more particularly to Hoffmann, or annular kilns. Subsections deal with the reconstruction of old kilns, the building of new kilns, the firing operation, and the question of heat economy.

ENAMEL KILNS WITHOUT MUFFLES.—L. Vielhaber (*Ker. Rund.*, **33,** 158, 1925). It is possible to fire enamel with generator gas, or oil, or towns gas, if the correct amount of excess air is admitted and steps are taken to avoid sulphur.

THE USE OF MUFFLE KILNS FOR THE "ARCHING" OF PLATE GLASS POTS.—P. d'H. Dressler and L. T. Strommer (*J. Amer. Cer. Soc.*, **8,** 216, 1925). A substantial economy of labour and fuel, and a 21% increase in the average life of glass pots, have been effected by preheating, or "arching" them in muffle kilns. A suitable kiln is described fully.

KILN STOKERS.—J. D. Martin (*J. Amer. Cer. Soc.*, **8,** 396, 1925). The method of applying kiln stokers to round down-draught kilns, firing refractories, is presented.

THE IMPORTANCE OF THE TUNNEL KILN IN THE BRICK INDUSTRY.—B. Ultsch (*Tonind. Ztg.*, **49,** 340, 1925). Some experiences are recounted with a Lengersdorff kiln firing bricks. The kiln is 92 m. long, holds 54 trucks each carrying 1,000 bricks, and fires 12,000 bricks daily. In spite of a high moisture content in the unfired bricks, the kiln has functioned admirably.

NEW ELECTRIC RADIATION FURNACES FOR CERAMIC PURPOSES.—A. Paolini (*Ker. Rund.*, **33,** 115, 1925). The graphite resistances can be brought to a temperature of 2,200°, and this heat is transmitted through special silicon carbide walls having large radiation flues, to the heating chamber. Sketches are given of various designs.

TURNING A POOR ENAMELLING FURNACE INTO A GOOD ONE.—H. F. Staley (*Ceramist,* **5,** 144, 1924). A kiln of the closed muffle type, which was very unsatisfactory for enamelling temperatures, was converted, at comparatively low cost, into an open muffle or semi-muffle furnace. The result was a great saving of fuel and greatly increased capacity.

FURNACE HEATING. V.—R. J. Sarjant (*Fuel,* **4,** 232, 1925). The subjects dealt with include the utilisation of waste heat, waste heat boilers, boiler testing, heat insulation, recuperation, heat treatment. Illustrations of various types of recuperators, regenerative furnaces, annealing furnaces, are given.

PRESENT AND FUTURE WALLS FOR USE AGAINST MOLTEN GLASS.—R. J. Montgomery (*J. Amer. Cer. Soc.*, **8,** 205, 1925). The future glass pot will be of good, white firing clays, uniform structure, fine grained and more refractory, with less impurities. The chem. comp. will be suited to the composition of the glass batch and the temperature of the furnace. The density will depend upon the fluidity of the molten glass.

FURNACE HEATING. II.—R. J. Sarjent (*Fuel*, **4**, 96, 1925). Temperatures of combustion, gas burners, combustion of solid fuels, control of combustion, and avoidable and unavoidable losses, are among the factors dealt with.

PLATINUM–RESISTANCE THERMOMETRY AT LOW TEMPERATURES.—M. S. van Dusen (*J. Amer. Chem. Soc.*, **47**, 326, 1925). A simple modification of the Callendar equation, which expresses accurately the resistance of platinum as a function of temperature on the thermodynamic scale throughout the range 0° to–190°.

ORGANIC GLASS.—W. Herzog (*Rev. Prod. Chim.*, **28**, 113, 1925). A short historical review is given, showing that the patents taken out by Pollak and Ripper were preceded in principle by others, notably by H. John, of Prague.

THE COOLING PROCESS IN HOFFMANN KILNS.—G. Paschke (*Deut. Töp. Zieg. Ztg.*, **56**, 328, 1925). Theoretical calculations are given which do not involve the use of the calculus.

LABORATORY EXPERIMENTS IN THE DEVELOPMENT OF A PLANT DRYER.—W. E. Barrett (*J. Amer. Cer. Soc.*, **8**, 239, 1925). Experimental dryers were constructed and tested, the data collected in drying bricks and tiles leading to the following conclusions: The drying medium must travel in a direction such that it strikes all the surfaces of the ware equally and in a positive manner; very rapid drying is possible if uniform shrinkage of the ware is maintained; 60 ft. per minute is the maximum velocity of the air for safe drying; drying may proceed much more rapidly if the tiles are heated to a high temperature. A type of dryer is shown which would be almost as effective as the Proctor dryer and much less costly.

FUEL CONSERVATION IN GLASS WORKS BY USING DRY GENERATOR GAS.—(*Ker. Rund.*, **33**, 313, 1925). The calorific value of generator gas varies inversely with its moisture content. Moist gas may be due to three causes; The use of damp fuel; unsuitable methods of introducing steam; formation of water vapour owing to damp foundations. These causes are briefly discussed.

Patents.

TUNNEL KILN.—J. and C. Damide (*Engl. Pat.*, 228,186, 23/1/25). The drying zone, between the entrance end of the kiln and the main heating zone, is heated by flues leading from an air-heating jacket around the cooling zone. Air for combustion is heated in a space beneath the trucks.

ANNULAR TUNNEL KILN FOR SALT GLAZING.—Woodall-Duckham Ltd., and A. M. Duckham (*Engl. Pat.*, 228,230, 20/10/23). Pottery ware is first heated approximately to glazing temperature, out of contact with the combustion products, and then passed into a kiln atmosphere containing salt vapours at glazing temperature. An annular kiln for carrying out the process comprises a muffle section, followed by a glazing section containing the gas inlets, and a cooling section.

GAS-FIRED KILNS FOR BURNING LIMESTONE, SILICON, ETC.—Dowson & Mason Gas Plant Co., J. Paton, and E. W. Mawby (*Engl. Pat.*, 234,310, 3/7/24). Unrestricted air passages are provided round the wall of a gas-fired kiln, above and below the gas ports. The passages open into air ports arranged in a sloping manner, so that the gas is drawn toward the centre of the kiln by the air currents. The air is preheated by being passed through an annular space surrounding the conical hopper at the bottom of the kiln.

TUNNEL FURNACES.—Koppers Coke Oven Co., Ltd. (*Engl. Pat.*, 228,383, 20/3/24). One series of baffles extends across the floor of the cooling zone of a tunnel kiln and deflect the cool air toward the roof. Another series depends from the roof of the preheating zone and deflects the hot air toward the floor.

TUNNEL KILN FOR FIRING POTTERY.—C. Royes (*Engl. Pat.*, 234,162, 5/2/24). The usual sectional lengths of a tunnel kiln are formed by a combination of arches united by cement or mortar joints. A number of inspection windows is provided in each arched section, so that, in case of a stoppage, the section responsible can be located and removed without damaging the rest of the kiln. A chamber is added at each end of the kiln to prevent loss of heat during the entry and exit of the trucks.

KAOLIN REFRACTORY.—I. Harter and A. M. Kohler (*U.S. Pat.* 1,530,260, 17/3/25). Granulated kaolin is burned to a temperature of at least 1,650° and then bonded with kaolin.

REFRACTORY FURNACE MORTAR.—B. C. Sellars (*Engl. Pat.*, 231,650, 11/3/24). About 10% of dried sodium silicate is mixed with a refractory material such as alumina, asbestos, fireclay, ganister, etc., to form a mixture which, mixed with water forms a mortar suitable for repairing furnaces.

BRICK AND POTTERY KILNS.—W. Simpkin and E. Evans (*Engl. Pat.*, 233,033, 30/1/24). A portion of the gases from the kiln is utilised to entrain a supply of air, and after mixing therewith is delivered to the fireplaces.

GLAZES, ENAMELS.

THE MELTING-POINT OF ENAMEL.—A. Otremba (*Ker. Rund.*, **33**, 201, 1925). The effect of the fluxes—fluorspar, cryolite, and sodium fluosilicate—upon the melting temperature was studied. Fluorspar does not exert a uniform fluxing effect; up to about 4% it acts as a flux; up to about 18-25% it raises the m.p., and then again acts as a flux up to about 50%, after which, up to 70% it raises the m.p. to 1,370°. Cryolite is a powerful flux up to 20%, further additions raise the m.p. vigorously. Sodium fluorsilicate acts as a flux up to 18%; between 20 and 30%, and 40 and 50%, the curve flattens, after which the m.p. rises steadily. At about 52% the m.p. of all the batches was about 970°.

SOME FORMS OF SULPHURING ON EARTHENWARE GLAZES.—T. A. Shegog (*J. Amer. Cer. Soc.*, **8**, 148, 1925). Insoluble sulphates may be introduced through the body, the glaze, the water, or the fuel. Soluble sulphates in the body are deposited on the surface of the ware during drying in the form of a crystalline scum, especially on corners and sharp edges, where evaporation is most rapid. This may cause "crawling," or "creeping" of the glaze, and "dry" edges on plates. A troublesome case of this nature on sanitary ware was cured by sponging the ware in the dry, clay state. Sulphur in the fuel is converted during the firing into sulphur dioxide and sulphur trioxide; the latter, in the presence of moisture, may be deposited in small vesicles on the saggars and the ware in the cooler parts of the kiln, and give rise to "polka-dot" sulphuring, small dull spots or rings. Each dot or ring marks the position where acid-laden moisture condensed on the ware during the initial stages of the firing in the glost kiln. It is possible to avoid this condensation by means of good mechanical draught. Both soluble and insoluble sulphates in the glaze may cause trouble since both will be dissolved by the melted glaze. A bisilicate glaze dissolves about 4% of sulphate, whilst a tri-silicate glaze can dissolve only about 2%, yet the effect of reducing the amount of silica in a glaze is nullified to a large extent by the fact that the lower the silica in the glaze, the more vigorous the attack of the glaze on the silicon of the body. It is not necessary for the glaze to be saturated throughout with sulphates; a film of saturated glaze may develop on the surface and may not have time to diffuse through it owing to the high viscosity. Unlike the "polka-dot" type of sulphuring, which occurs early in the glost firing, the scum, or film type takes place later, when the kiln temperature is too high to allow condensation of moisture on the ware. It has frequently been found in practice that sulphuring is caused by repeated use of the same water in the glaze mills when soluble sulphates are used to float the glaze. Soluble sulphates

may be present in an earthenware glaze containing about 2·5 equiv. of SiO_2 to the extent of 40 grains per gallon (calculated as H_2SO_4) without harmful effects under normal firing conditions. A very slow kiln draught and a long glost fire are likely to produce sulphuring in either form when under normal firing conditions it would not occur. The roughening and darkening of the glaze which sometimes occurs in the decorating kiln is also a sulphur effect developed under the reducing conditions, which usually prevail almost to the end of the fire in this kiln. The sulphates are reduced to sulphites, at least near the surface of the glaze, and minute bubbles of oxygen are formed in the soft glaze, giving it the rough appearance. The dark discoloration is due to the reduction of lead in the glaze. This effect appears only in the hottest parts of the kiln. It may be regarded as a kind of surface spit-out due to sulphur. Sulphur, however, is not the usual or common cause of the ordinary form of spit-out, since this fault occurs in many cases when there is no indication of sulphuring.

OBSERVATIONS ON PIN-HOLING IN CAST WARE.—R. W. Hemphill (*J. Amer. Cer. Soc.*, **8**, 145, 1925). Dampness may cause pin-holing in a variety of ways. Damp moulds will cause pin holes, since they will not properly absorb the air out of the slip when it is first poured in. If cast ware is covered with very damp cloths, pin-holes will frequently occur where the ware and cloths are in contact. A case of this kind was cured by covering the ware first with dry cloths, wet cloths being then placed over them. Insufficient ball clay in the body may also lead, directly or indirectly, to pin-holing. In one instance, a slip was found to dry too slowly in the moulds; the ware would have the correct thickness after casting, but it would remain soft in the mould, and was full of pin-holes. The addition of a small quantity of dark ball clay cured these defects. Ware which gave good results when the ball clay content was as high as 23% was covered with pin-holes on reducing the ball clay to 10%. Other important factors are: sponging when the ware is leather hard; removal of all dust, either by blowing it off, or by dipping the cold ware in water at room temperature. The ware must then be dried thoroughly after the dipping or sponging, before the glaze is applied, and again after the glazing operation.

AVENTURINE GLAZES.—V. K. Haldeman (*J. Amer. Cer. Soc.*, **7**, 824, 1924). The effect of substituting chromic oxide for ferric oxide and alumina in a cone-02 aventurine glaze was studied. The substitution of lithium oxide for sodium oxide in the RO member was also investigated, as also the effect of variation in the boric oxide content. The base glaze used was:

$$1\ Na_2O \left\{ \begin{array}{l} 0{\cdot}1\ Al_2O_3 \\ 0{\cdot}85\ Fe_2O_3 \\ 1{\cdot}5\ B_2O_3 \end{array} \right. \quad 6\ SiO_2$$

To counteract the increased refractoriness and viscosity produced by the addition of chromic oxide, lithium oxide was substituted for Na_2O and the SiO_2 reduced, and the sum of the iron and chromic oxide was also decreased:

$$\begin{array}{l} 0\text{–}1\ Na_2O \\ 0\text{–}1\ Li_2O \end{array} \left\{ \begin{array}{l} 0{\cdot}1\ Al_2O_3 \\ 0\text{–}0{\cdot}75\ Fe_2O_3 \\ 1{\cdot}5\ B_2O_3 \\ 0\text{–}0{\cdot}75\ Cr_2O_3 \end{array} \right. \qquad 4\ SiO_2$$

A further series was tried, in which the glaze became:—

$$1\ Na_2O \left\{ \begin{array}{l} 0{\cdot}1\ Cr_2O_3 \\ 0{\cdot}65\text{–}0{\cdot}9\ Fe_2O_3 \\ 1{\cdot}25\text{–}2{\cdot}0\ B_2O_3 \end{array} \right. \qquad 4\ SiO_2$$

In addition, several different heat treatments were tried, in order to determine the firing temperature and the rate of cooling which promoted maximum crystallisation.

Substitution of chromic oxide for iron oxide in this glaze even in small amounts (0·1 equiv.), was found to decrease the fluidity to such an extent

that crystal development is prevented entirely with a low boric oxide content. Even with a high boric oxide content, the crystals are too small. Replacing the alumina by 0·10 equiv. of chromic oxide also gives crystals which are not readily visible. Replacing the alumina by 0·05 equiv. chromic oxide changes a high iron aventurine from an excessively crystallised rough, matt glaze to one of high gloss with attractive crystals. The results indicated that the addition of 0·01 to 0·02 equiv. of chromic oxide to a high iron aventurine would produce an excellent glaze. The substitution of lithium oxide for sodium oxide is definitely detrimental to aventurine formation; it produces a micro-crystalline structure, and in combination with chromic oxide, excellent matts. A high content of chronic oxide results in crazing, which is further encouraged by high contents of boric oxide and lithium oxide. No advantage is gained by firing to a temperature higher than the maturity range. A rapid oxidising fire is desirable ; slow firing may lead to volatilisation of boric oxide. Best results were always obtained by allowing the kiln to cool without attempting to regulate it. No increase in crystal development was observed by holding the temperature for different periods at temperatures varying from 700 to 1,100°.

MICROSCOPICAL DETECTION OF SULPHUR EFFECTS ON EARTHENWARE GLAZES.—A. Schoblik (*Ker. Rund.*, **32**, 663, 1924). In firing lead-glazed earthenware, the flame is maintained as clear as possible. If, for fear of smoking the ware, this oxidation is carried to excess, any sulphur compounds present, even in small quantities, will often seriously affect the glaze. In a strongly oxidising atmosphere, the sulphur present in the form of sulphides becomes converted into sulphuric acid. This compound does not leave the kiln, but penetrates into the glaze. The latter then becomes matt, or, in bad cases, becomes coated with a white deposit which, even when carefully removed by washing with water, rapidly reappears of itself. If sulphur is already present in the biscuit ware, alternating periods of reduction and oxidation must be rigorously conducted during the glost fire if the effect is to be thoroughly eliminated. If a glaze which has been sulphured during the glost fire, or during cooling, and has become slightly matt, is examined in thin section under the microscope, it will be observed that the matt portions are formed of innumerable minute, needle-shaped crystals, which have collected at the surface. In more pronounced cases of sulphuring, the glaze becomes matt throughout. Under the microscope, small blisters are observed, between which innumerable particles of clay substance and, here and there, small crystals are embedded. Sulphuric acid, being the more powerful, expels the boric acid at this high temperature, thus causing supersatuation to take place. Furthermore, other sulphates are liberated and in this manner the melting point of the glaze is raised considerably. The elimination of such a fault during the firing of the kiln is, of course, impossible, the quantity of fluxes having become too small. If the sulphuring is still more serious than in the above-mentioned instances, the glaze will seem to have disappeared entirely, and the ware will appear to be covered with a white powder, which can readily be removed. This powder is composed of partially crystallised sulphates and clay substance. These crystals are so minute, that very powerful magnification has to be employed to detect them. A fault of this nature cannot be cured. A crazed glaze is the commonest form of sulphuring. In this case the surface of the glaze is very uneven and is full of blisters and precipitated matter. Microscopically, this type of glaze is easily distinguished from faulty glazes of other kinds. Characteristic blisters are always present, and these rarely exhibit the normal circular form. This peculiar blister formation is brought about by the deposition on and about the gas bubbles of precipitated sulphates, which are insoluble in the glaze. Usually, these precipitates assume a lattice-like formation. The sulphur in pyritic saggar bodies cannot be eliminated in a single fire ; as a rule, several firings are necessary. To prove this, a small quantity of pyrites was added to a saggar body. After firing glazed ware in a saggar made from this body, the ware came out badly crazed. Even

after a third fire, the glazed ware still showed signs of sulphuring, although the lattice formation appeared much finer under the microscope. Glazes containing considerable amounts of sodium sulphate have a uniformly matt appearance. The cause of this is the sodium itself which volatilises at high temperatures. The effect is a shrivelled glaze, which exhibits under the microscope distorted blisters and precipitates characteristic of sulphuring. With a glaze containing approximately the same amount of calcium sulphate, the sulphur effect is so small that the glaze appears to be faultless. In thin section under the microscope, however, the influence of sulphur at once becomes apparent.

The results obtained in working out a method for detecting the faults in question may be summarised thus: If distorted blisters are observed in the thin section, this may be taken as definite proof of the action of sulphur. Blisters or bubbles must also be present, even if the glaze is not completely "dry," or if the effect has not been produced until right at the end of the burn, or even during cooling. In the second case, the glaze has melted properly, but the surface is covered with a dull film, which can be wiped off, but which rapidly reappears. Under the microscope, small needle-like crystals are visible in this case. With crazed glazes the degree of sulphuring can be gauged by the size of the lattice formation, the amount of precipitation and the number of gas bubbles.

COLOURS IN A ZINC–SILICATE GLAZE.—Kraner (*J. Amer. Cer. Soc.*, **7**, 868, 1924). In a new method, by which the fritting of the glaze is obviated, the soluble sodium content is introduced in the form of sodium silicate. The latter substance, having a specific gravity of 1·48 and containing 13·7% soda, 32·9% silica and 53·4% water, is not absorbed to any appreciable degree by biscuit whiteware or faience of 10% porosity. When used as a sou rce of Na_2O and SiO_2 in a glaze of the willimite type, this compound does not affect the fusion properties of the glaze. The glaze may be prepared in a mortar , in a paint mill, or in a ball mill, and grinding does not appear to be essential to obtain good results. The glaze may be applied either by means of a brush, or the piece may be dipped in the usual way. After drying on the ware, the glaze is hard and tough and the piece can, therefore, be handled safely. Tiles may be stacked one upon the other without danger of the glaze coating. The effects were studied of seven colouring oxides, viz., those of cobalt, nickel, manganese, copper, uranium, iron and chromium, upon a typical glaze with the following batch composition: sodium silicate 150·18, flint 58·8, zinc oxide 54·27, titanium oxide 24·0 and water 15·0, the molecular formula being: $0{\cdot}33\ Na_2O\ \ 1{\cdot}8\ SiO_2$
$0{\cdot}67\ Zn_2O\ \ 0{\cdot}3\ TiO_2$

The colours were added to this glaze and not substituted for another RO in the formula. The glaze and colour were milled together for two hours in one-gallon laboratory ball mills. Specimen tiles were fired in a tunnel kiln to cone 9 half down in 17 hours. The ware was exposed to the direct action of the gases, oxidising conditions being maintained throughout. All the possible two-and-three-colour combinations were tried with each colour, two series being investigated, one with a moderate concentration of colour, the other with a strong concentration. A somewhat rapid rise in temperature from about 1,000° to the maturing temperature appeared to have a more important bearing upon crystallisation than did slow cooling. Interesting developments of colour in crystals were obtained by blending glazes containing less than 0·05 molecular equivalents of colouring oxides, and interesting textures and some unusual backgrounds were observed among the mixtures containing a total colour concentration of 0·10 mol. equiv. Absorption of colour by the crystals took place in the following descending order: cobalt in large amounts, the brown colour of the background being intensified; copper is retained by the glaze, the green colour being entirely absorbed by the crystal; manganese is not absorbed so much, nickel and iron are similar in their action, but the former tends to prevent crystallisation at about 0·05 mol. equiv., whilst FeO may be added up to 0·2 mol. equiv.; uranium is not absorbed to any

appreciable extent, but under reducing conditions, black or bronze coloured crystals can be obtained with 0·10 equivalents; chromium cannot be used as a colouring medium in this glaze, since it prevents crystallisation, even when present to the extent of only 0·01 mol. equivalents.

AN ALALYSIS OF THE SUSPENSION OF ENAMEL BY CLAY IN TERMS OF THE COLLOID THEORY.—E. P. Poste (*J. Amer. Cer. Soc.*, **8,** 232, 1925). A general review of the literature (mainly American), on the colloid theory is given, the object being to formulate a statement to elucidate the process of enamel formation by the wet method.

THE CHEMICAL RESISTANCE OF ENAMELS.—W. Athenstaedt (*Emaillew. Ind.*, **1,** 137, 1925). Some general considerations are given.

MAJOLICA ENAMELS.—L. Vielhaber (*Emaillew. Ind.*, **1,** 8, 1925). A suitable enamel contains : 27·3% borax, 57·4% red lead, 7·55% soda, 25·11% quartz. The following colours are added for powder enamels : green—1·5% iron oxide, 1% copper oxide, 0·25% chromium oxide; brown—1·5% red iron oxide, 0·5% pyrolusite ; blue—0·5 cobalt oxide, 0·2% pyrolusite. A rule for majolica enamels is :—

$$PbO = \frac{29{\cdot}27 - R_2O}{0{\cdot}38} \text{ or } R_2O = (79{\cdot}4 - PbO) \times 0{\cdot}38.$$

A STUDY OF FLUORINE COMPOUNDS IN WHITE ENAMELS.—J. W. Permann (*Emaillew. Ind.*, **1,** 43, 1925).

PRINCIPLES OF ENAMELLING. VI.—EFFECT OF THE SIZE OF GRAIN OF FELSPAR ON THE MELTING OF ENAMELS.—H. F. Staley (*Ceramist*, **1,** 29, 1925). The time required to melt a batch containing 40-mesh felspar is 28% longer than that necessary if the felspar is ground to 140-mesh. With 90-mesh material, it takes 12½% longer, whilst with 200-mesh felspar practically the same times is necessary as with 140-mesh material. A blue tint is developed in lead oxide—antimony enamels containing coarse felspar owing to the length of time required to melt the batch.

MAKING AND BURNING OF GLAZED WARE. XIX. FRITS.—(*Brit. Claywr.*, **34,** 40, 1925). Continuation of a lengthy article. Glazes containing tin oxide are discussed.

A MICROSCOPIC STUDY OF STRESSES IN GLAZES.—A. V. Henry (*J. Amer. Cer. Soc.*, **8,** 117, 1925). An effort was made to determine to what extent the stresses in a glaze are due to differences in the coefficients of expansion between body and glaze. The theory relating to glasses under internal stress(*cf.* Adams and Williamson, *J. Wash. Acad. Science*, **9,** 1919), was applied in the experimental work, the difference in the optical path of rays of light passing through a glaze being measured by means of a microscope and a compensated quartz wedge. Values obtained experimentally on a number of tile glazes representing variations in birefringence or stress multiplied by a constant are plotted in curves. It is concluded that differences in the coefficients of expansion between body and glaze are the chief causes of stresses in glazes. At ordinary temperature, the glaze should preferably be under slight compression.

IMPROVEMENT IN THE ETCHING PROCESS OF SHEET IRON.—W. Athenstaedt (*Emaillew. Ind.*, **1,** 93, 1925).

OPACIFYING MEDIA CONTAINING FLUORINE.—A. Otremba (*Emaillew. Ind.*, **1,** 33, 1925 ; *Ker. Rund.*, **33,** 343, 1925). The opacifying effects of felspar, fluorspar, cryolite (natural and synthetic), and sodium fluosilicate were studied. The results of 9 series of tests, involving a large number of meltings, are tabulated.

OBSERVATIONS ON "HAIRLINES" IN SHEET IRON ENAMELS.—J. E. Hansen and G. S. Lindsey (*J. Amer. Cer. Soc.*, **8,** 356, 1925). "Hairlines," as distinguished from the fine cracks in a crazed enamel, are fine dark

lines which appear where the dark ground coat shows through the cover enamel. They are caused by underfiring the ground coat, or by "cold spots" when the ware is in contact with, or in close proximity to, cold objects while the cover coat is being fired. An underfired ground coat may be the result of too short a firing period, of too low a temperature, or of too thick enamel.

A METHOD OF CONTROL OF ENAMEL FOR DIPPING FLAT WARE—K. R. Fusselbaugh and B. T. Sweely (*J. Amer. Cer. Soc.*, **8**, 303, 1925). To ensure uniformity in the application of the ground coat of enamel to steel the specific gravity of the slip and the degree of fineness of the material must be carefully controlled. All materials introduced in the mill charge must be weighed accurately, the operation of the mill controlled by means of a revolution counter, the degree of fineness checked by sieve analyses, and the specific gravity corrected regularly to a predetermined standard. A simple method of standardising the milling process is described.

GLAZES COLOURED BY MOLYBDENUM.—W. E. Barrett (*J. Amer. Cer. Soc.*, **8**, 306, 1925). A porcelain body containing 38% ball clay, 29·5% felspar, 32·2% flint, and 2 and 3% MoO_3, fired to cone 12, had a bluish-green colour. A bright yellow colour was secured when varying percentages of molybdenum oxide were added without grinding to a bright and to a matt glaze. Small additions of molybdenum have a strong colouring action.

COLOURS, DECORATIVE PROCESSES, ETC.

THE APPLICATION OF COLOURED ENAMEL DECORATIONS TO UNGLAZED WARE.—(*Diamant*, **46**, 316, 1924). The unglazed ware is first dipped in a 25 per cent. ammonium carbonate solution. This not only removes dirt, etc., from the ware, but prevents the body from absorbing moisture from the enamel, which, therefore, remains more fluid and adheres better to the ware. A considerable amount of clay must be mixed with the enamel. The ware is dried and fired in the usual way.

PHOTO-LITHOGRAPHY APPLIED TO CERAMICS.—C. Fleck (*Sprech.*, **58**, 2, 1925). The subject is treated under the following headings: (1) direct transfer methods, (*a*) by the chromate-albumin process; (*b*) by the enamel copying process, and (*c*) by the asphalt copying process; (2) indirect transfer methods by means of (*a*) albumin or gelatine paper, and (*b*) photographic printing. Recipes are quoted for the various processes.

A SLIP PAINTING PROCESS.—D. W. Cox (*J. Amer. Cer. Soc.*, **8**, 310, 1925). A method is described by which a craftsman with limited equipment can produce one-fire common stoneware decorated by a slip painting process.

POTS AND PINES, A DECORATIVE PROBLEM FOR THE ARTIST POTTER.—M. K. Cable (*J. Amer. Cer. Soc.*, **8**, 393, 1925). A method of producing a soft green pine tree vase is outlined.

Patents

COATING PORCELAIN, ETC. (WITH METALS).—A. F. Eijssen (*Engl. Pat.*, 229,263, 28/11/24). Porcelain on glass is coated with brass, etc., by rubbing the dulled surface with a small quantity of glycerol by means of a brush of brass or similar material. Other metals may then be deposited electrolytically on the coated article. If silver is desired in the deposit, silver nitrate may be added to the glycerol.

DECORATING POTTERY.—N. H. von Lerven (*Engl. Pat.*, 230,587, 16/1/24). A stencil is formed by moulding a transparent substance (solution of cellulose-esters, viscose, casein, collodion, etc., in acetone, etc.), upon a model of the article to be decorated. The layer on the model is perforated along the outlines of the design, is then cut through vertically to permit removal, and is applied to the object, carbon being dusted through the perforations.

PLANT AND MACHINERY, ETC.

POLISHING PORCELAIN.—O. Ballentin and C. Krug (*Ker. Rund.*, **33**,

263, 1925). A few notes on the polishing, or grinding of porcelain pieces, *e.g.*, insulators, are followed by a description, with illustrations, of several machines.

INDIVIDUAL OR GROUP DRIVE.—K. W. Drake (*Brick*, **66**, 594, 1925). The advantages and disadvantages of the two systems are discussed, examples being given and illustrated.

THE DIESEL ENGINE.—R. H. Bacon (*Brick*, **66**, 598, 1925). The operation of the Diesel engine is described and reasons are given in support of its claim to be considered good equipment.

THE A.E.G. OPTICAL PYROMETER.—(*Sprech.*, **58**, 161, 1925). A description is given of a smaller and cheaper type of the well-known A.E.G. pyrometer.

SUGGESTIONS FOR THE FURTHER DEVELOPMENT OF THE CERAMIC VISCOSIMETER BY DR. KOHL.—E. P. Bauer (*Sprech.*, **58**, 169, 1925). The Fischer-Bauer viscosimeter is described.

THE MECHANISM OF FILTRATION ; STUDIES ON THE LEAF SUCTION FILTER.—B. W. Clarke, S. G. M. Ure, and J. W. Hinchley (*Chem. Tr. J.*, **76**, 131, 1925). The theory of the subject, as treated in the literature, is reviewed. Preliminary work has been carried out in the Chemical Engineering Laboratories at the Imperial College, London. A suitable leaf filter was divised for the purpose, magnesium carbonate, calcium carbonate, and barium phosphate, precipitated under definite conditions, being used in the experiments. These compounds were either crystalline or composed of rigid particles, and there was no evidence of consolidation of the cake under increasing pressure of filtration in the vacuum method. Similar experiments were also carried out with a plate-and-frame filter press. In this case a definite progressive increase in the percentages of solids in the cake as the pressure increased was noted. There is a progressive increase in the percentage of solids in the cake as the percentage of solid matter in the prefilt diminishes and the time required to form the cake increases as the strength of the prefilt diminishes, *i.e.*, the thinner the slip, the less water in the cake, but the longer the time required to press up. The resistance offered by ordinary filter cloths was determined on three types, viz. : (1) a heavy cloth, chain weave, 40×40 strands per sq. in. ; (2) fine cloth, twill weave, 70×70 strands, and (3) monel metal cloth, special weave, 10×250 strands. The figures (minimum and maximum) were :

Cloth.	Pressure in lb. per sq. in.	Rate of Flow in cc. per min.
1	0·60	nil.
	13·20	6060
2	0·50	nil.
	12·10	9540
3	0·70	750
	11·15	10850

If the cake is thicker than $\frac{3}{4}$ inch, the rate of flow is directly proportional to the pressure, but for thinner cakes, the flow depends upon some power of the pressure. Fluctuations in the pressure, the use of cloths after having been washed, and the absorption by the cloths of impurities in the water appeared to increase rather than to diminish the cloth resistance.

AIR SEPARATION IN GRINDING AND PULVERISING.—C. S. Messinger (*Chem. Tr. J.*, **76**, 451, 1925). The principles and applications of the "Raymond" System are described (2 illustrations).

THE HEATING OF ROOMS.—M. Fishenden and R. E. Willgress (*Fuel*

Research Board, Tech. Paper, No. 12). Experiments were carried out with the object of determining the relative costs of providing sufficient energy to keep the occupants of a room comfortably warm under different methods of heating.

RUBBER GRINDING MILL LININGS.—B. W. Rogers (*J. Amer. Cer. Soc.*, **8**, 326, 1925). Rubber linings in ball mills gave 20% more capacity, 10% less power consumption, and 0·9% more 200-mesh material than steel linings. Other advantages are : decreased mill weight, reduced maintenance cost, minimum contamination of charge, and possibility of jointless, detachable sections (*cf. Trans.* **23**, 71A, 1924).

TRIMMING REFRACTORY BRICKS AFTER FIRING.—C. Grupp (*Tonind. Ztg.*, **49**, 351, 1925). A machine for grinding—or milling—fired refractories is illustrated and described. It is adjustable both vertically and horizontally and is supported on steel-headed rails. The milling is done by cylindrical, profile, or side milling cutters, made of silicon carbide, or of a steel core coated with silicon carbide.

THE DEVELOPMENT OF THE HARDINGE MILL.—J. C. Farrant (*Chem. Age*, **12**, 300, 405, 1925). Particulars of the development and improvement in design of the Hardinge mill in the Eastern Hemisphere, together with operating data, are given.

DATA ON THE PULSICHROMETER.—R. Galbraith (*J. Amer. Cer. Soc.*, **8**, 59, 1925). A table is given showing the plate openings to be used with enamel and slips of different weights in order to reduce the skill required to obtain a smooth, even coating. A large orifice does not develop enough back pressure to give the enamel sufficient velocity through the tube.

Patents

BRICK-MAKING MACHINE.—R. Hickton and W. Bagguley (*Engl. Pat.*, 218,876, 29 Aug., 1923). In a machine such as described in *Spec.* 165,120, the mould is carried by slippers running on tie rods connecting brackets. A table, integral with the mould, receives a cut length of extended clay, which is passed thereto over an oiled roller. Upon advance of the mould, the clay is pressed within the mould and against a fixed die carried by the bracket, and is ejected, upon withdrawal of the mould, by a bottom plate.

TRANSPORTING EARTHENWARE PIPES.—A. H. Owens (*Engl. Pat.*, 231,671, 9/2/24). Apparatus is described for transporting socketted earthenware drain pipes from a vertical press to the drying floor, and for inverting them.

DRYING CHAMBER.—P. Kiess (*Engl. Pat.*, 232,851, 11/9/24). A pipe, which doubles back upon itself, extends down the centre of a drying chamber and is connected with furnaces outside the chamber, the ware being conveyed on trucks on either side the pipe.

III.—FINISHED PRODUCTS: TESTING, ETC.

THE THERMAL CONDUCTIVITY OF CARBORUNDUM REFRACTORIES.—M. L. Hartmann and O. B. Westmont (*J. Amer. Cer. Soc.*, **8**, 259, 1925). See Abstract Trans. **23**, 99A, 1924).

CONDUCTIVITY AND SPECIFIC HEAT OF REFRACTORIES AT HIGH TEMPERATURES.—M. D. Hersey and E. W. Butzler (*Ceramist*, **1**, 36, 1925). The problem is stated in general terms, and results are given on Georgian firebricks up to 910°. An example is given illustrating the meaning and application of the conductivity data.

CHANGES IN THE MICRO-STRUCTURE OF PORCELAIN AND SOME OF ITS PHYSICAL PROPERTIES DURING THE BURNING PROCESS

IN A TUNNEL KILN.—E. Kempcke (*Keramos*, **3**, 551, 1924). With the help of the microscope the course of the formation of porcelain, above a temperature of 1,000°C., the inter-action of the raw materials upon each other, and the changes in the structure of porcelain, together with an investigation of some of the physical properties during the firing process in a tunnel kiln, were studied. A gas fired tunnel kiln had to be closed down for some technical reason. Samples of porcelain were taken from each of the trucks after a uniform cooling period of 48 hours, beginning with a sample which had been burning to over 1,000°, and proceeding in intervals of 25 to 60°. Porcelain plates 12 cm. diameter and cups 8 cm. high were taken out, and from these square pieces were cut out of the middle as near as possible. The body corresponded to the composition of 47·5% clay substance 26% quartz and 26·5% felspar. The glazed on the pieces corresponded to the formula

$$7{\cdot}6\ SiO_2\ \ 0{\cdot}73\ Al_2O_3 \left\{ \begin{array}{l} 0{\cdot}70\ Fe\ O.\ \ CaO.\ \ MgO \\ 0{\cdot}30\ K_2O,\ Na_2O \end{array} \right.$$

The pieces were submitted to physical tests, including the determination of the colour and hardness of the body and glaze, of the fracture, the porosity, and the true and apparent specific gravity. In order to examine the changes in the micro-structure of the test pieces during the firing process, thin sections, cut perpendicularly through body and glaze, were prepared. These sections provided data, not only on the structure of body and glaze, but also on the transitional layer between them. The samples which had been fired to 1,050 to 1,160° appeared to be dry, non-transparent products like earthenware. Evidence of sintering only began to appear at the corners and in thin parts of samples at 1,180°, whilst at 1,230° they exhibited almost the character of porcelain. Thin sections of porcelain fired at 1,120 and 1,160° showed the development of bubbles which were formed by the evolution of CO_2 from the decomposed carbonates. At 1,160° a few crystals of calcium-meta-silicate and mullite were observed but at 1,180°, the latter crystals had increased greatly in number owing to the melting of the felspar. Numerous clearly defined clusters of crystals were seen to have developed in a glassy matrix ; porcelain formation had begun and it continued with increasing solution of the quartz and crystal formation until at 1,420° it reached its maximum, showing a glassy ground mass, full of a felted network of crystals.

TERRA COTTA BODY INVESTIGATION.—B. S. Redcliffe (*J. Amer. Cer. Soc.*, **7**, 834, 1924). Five American clays were the subject of an investigation to determine their suitability for terra cotta purposes. Ordinary grog, and also grog made by calcining the clays to cone 2-3, were mixed with the clays. Test pieces were made and the various bodies tested for shrinkage, absorption, modulus of rupture, cool-cracking (quenching from 400° to 0°) and spalling. It was found that it would be difficult to give preference to any individual kind of grog ; 8 to 40-mesh grog bodies gave the best results in the quenching test. Bodies having a modulus of rupture above 1,800 did not withstand the cool-cracking test, whilst those below this figure gave good results in this respect. The chemical analyses indicated that the Al_2O_3—SiO_2 ratio was of great importance. A clay with 27·42 Al_2O_3% and 57·82% SiO_2 was much superior to one containing 23·67% Al_2O_3 and 60·87% SiO_2.

PROPERTIES OF THE TECHNICAL PORCELAIN MADE AT THE STATE PORCELAIN WORKS, BERLIN.—Rieke (*Zeit. angew. Chem.*, **37**, 190, 1924). Berlin and other types of porcelain were tested for tensile strength, localised crushing strength, resistance to bending strain, and resistance to impact bending stress. The tensile strength was measured on specially shaped specimens. The localised crushing strength was determined on circular plates, 10 cm. in diameter and 1 cm. thick, which were placed between two steel balls, 31·7 mm. in diameter, pressure being applied slowly until the discs—usually 4 or 5 at a time—broke to pieces. The resistance

to bending strain was measured on cylindrical rods 120 mm. long and 16 mm. diameter. For the determination of resistance to impact bending stress, a machine with a swinging hammer, specially made for testing ceramic products, was used ; the test pieces were 12 cm. long and 16 mm. in diameter. Eight different kinds of commercial technical porcelain were examined, and the results show that the highest values were obtained in every case for the Berlin porcelain. The following table gives the average figure for 5-10 tests :

	Tensile Strength kg./sq. cm.	Localised crushing Strength kg.	Bending Strain kg./sq. cm.	Impact bending Stress cm. kg./sq. cm.
Berlin technical porcelain ..	320	1376	855	1·99
Seven other types ..	161–265	675–1384	588–777	1·75–1·95

The Berlin porcelain shows very high values for tensile strength and bending strain ; the impact bending strength, which is a measure of the brittleness or toughness of the material, is also high for the Berlin product, and is only exceeded by steatite bodies. According to recent work by Steger, the modulus of elasticity of Berlin porcelain is 8,280 kg.sq. mm. The glaze is highly resistant to chemical action. A mixture of 65 parts water, 25 parts conc. sulphuric acid, and 10 parts cnc. nitric acid was boiled down until all the H_2SO_4 had volatilised, and even after this test had been repeated ten times, the glaze on Berlin porcelain had not been affected to the slightest degree. Strongly alkaline solutions, however, dissolve small quantities of the highly silicious glaze after lengthy treatment.

The modern tendency is to devote more and more attention to the microstructure of porcelain, and the results hitherto reported justify the conclusion that the examination of thin sections will yield important data on the quality of porcelain. An unmistakeable relationship is apparent, between the mechanical properties and the quantity of free quartz present in a porcelain body. The best porcelain is one which shows in thin section only traces of free quartz grains. The degree of sillimanite formation is also an important factor in this respect. Porcelains of this type, which have to be fired to very high temperatures to produce these results, also prove to be the best from the point of view of electrical insulation.

CONTRIBUTION TO THE BETTER KNOWLEDGE OF HIGH TENSION PORCELAIN.—K. H. Reichau (*Ker. Rund.*, **32**, 531, 1924). The first requirement of an insulator material is, that it must be absolutely dense and must show a glassy and not granular fracture like sand-stone. This requirement, which is so easy to fulfil in the case of thin porcelain ware, becomes one of the most difficult demands to satisfy when it is a question of manufacturing thick porcelain pieces. To test whether it was possible to produce a dense porcelain by increasing the amount of flux, three bodies, properly compounded and physically identical, containing 30%, 35% and 40% respectively of felspar, were fired to different temperatures. It was then seen that the tough wavy fracture of true hard porcelain disappeared in proportion as the felspar content increased ; it changed to the conchoidal fracture of felspar and finally to the smooth, greasy fracture of felspar glass. For several reasons such bodies with high felspar content are not suitable for high tension insulators. In the first place, these short bodies are difficult to work in the green state and it is extremely difficult to fire satisfactorily pieces varying in thickness with this material, because the thinner portions

of the piece begin to melt before the thicker parts have been properly fired, and finally, because such insulators are very susceptible to changes of temperature. Resistance to sudden change of temperature is a second important requirement. In general, coarse-grained materials are much less sensitive to sudden temperature changes than fine-grained materials having identical coefficients of thermal expansion. This is because the internal stresses cannot readily be equalized in a fine-grained material. Insulators with granular fracture like earthenware represent, technically, a compromise between these two demands. The latter, however, can only be fulfilled simultaneously by a material which is entirely homogeneous in all its parts. Such homogeneous porcelain is known in the technical sense as genuine or ideal porcelain. The material of which the high tension insulators are made must be genuine, or as nearly as possible genuine porcelain. In fulfilling these two demands, other requirements such as those of great mechanical strength, great elasticity and high dielectric resistance are automatically satisfied. In addition, another valuable property is automatically secured, namely, inner-chemical stability, which is a guarantee against ageing of the material. In preparing the green body, the raw materials, kaolin, quartz and felspar, usually in the relationship of 50 : 25 : 25, are finely ground and thoroughly mixed with water to a plastic mass. During the firing the kaolin loses its water at about 500°C. (100 parts of kaolin contain about 14 parts of water) and undergoes molecular decomposition into silica and alumina. At about 900° part of the free silica appears to combine with the alumina to form an amorphous silicate of the composition $Al_2O_3SiO_2$ or an amorphous sillimanite. At about 1,100° to 1,200° the felspar begins to soften and at still higher temperatures begins to act as a solvent on the other components, namely, silica, alumina and the amorphous sillimanite. In order to render this action as intensive as possible, the body must be correctly prepared. First, the various components in the body must be present in the correct form and grain size in order that the ingredients may offer the greatest possible molecular surface to the solvent attack of the felspar. Further, the body must be able to withstand long firing at high temperatures. The higher the firing temperature and the longer the firing period which the body can withstand, the greater is its value, because in such a body the felspar has been able to react more completely upon the different ingredients. Microscopic thin sections of the finished porcelain body show clearly whether this re-action has been completed or not. If the thin section shows a large quantity of free quartz in the form of tiny splinters, of if many angular fragments are visible, it may safely be concluded that the porcelain is more or less porous, or that it has a high felspar content. If, however, the re-action is complete, the thin section will exhibit a homogeneous glass with innumerable minute crystals of sillimanite showing a partially latteral structure. Such a porcelain is entirely homogeneous and is known in the technical sense as a genuine porcelain.

Practical tests on Hewlett Suspension Insulators prepared from such a body and measuring 22 cm. in diameter gave the expected results. A third requirement of high tension porcelain is, that it should possess sufficiently high dielectric strength. For several reasons, a thin flat unglazed plate, measuring 10×10 cm., is used for testing purposes. If a plate of this kind can be fired well and without distortion, this proves that the body is homogeneous throughout, that it has uniform shrinkage and that, therefore, insulators made from it will be free from internal stresses. The apparatus for this test is described. Finally, the porcelain material must be highly resistant to tension, pressure and impact. In considering the figures obtained for mechanical strength of porcelain (tension, pressure and impact) it must be remembered that they are relative only. In all cases the greatest importance should be attached to the resistance to tension, because this test gives an indication as to the extent to which the ingredients forming the porcelain have been bound together by the manufacturing processes. The other

figures will be valued according to the mechanical demand to be made on the particular type of insulator in practice. A simple method of obtaining at least one indication of the quality of hard porcelain is indicated. Since the quality of the porcelain depends in the first instance, upon more or less complete and uniform formation of sillimanite crystals in the porcelain body, and since these sillimanite crystals contained in the quartz-felspar matrix of the porcelain are much more resistant to the chemical action of hydrofluoric acid than the glassy matrix in which they are embedded, the resistance of the porcelain body to the action of hydrofluoric acid will give an indication of the amount of sillimanite crystals present in the porcelain.

Another means of obtaining information on the structure of porcelain bodies, especially their content of free quartz, is by means of the mineralogical microscope, preferably with Dr. Köhler's arrangement for the production of circularly polarized light. Under circularly polarized light between crossed nicols, all the free quartz content in a thin section of porcelain body appears more or less light against a dark background, and from the quantity and especially the character of these quartz grains, or simply from the general appearance in natural and polarized light, important conclusions may be drawn regarding the composition, the firing and the properties to be expected of the finished porcelain.

THE REFRACTORY-UNDER-LOAD TEST AND ITS POSSIBILITIES.—H. Hirsch (*Ber. deut. ker. Ges.*, **5**, 65, 1924). Previous work on the softening-point test is reviewed fully. Tests were carried out partly with the aid of a new machine (*cf. Trans.*, **23**, 47A, 1924). The pressures applied were 1 kg/sq. cm. for silica bricks, and 2 kg/sq. cm. for grog bricks, these being found by experiment to be the most suitable. The effect of composition ($Al_2O_3 : SiO_2$ ratio) was brought out clearly by observation of the temperature at which the samples collapsed rapidly. The kaolins were in a group by themselves, since they did not give uniformly sloping curves. Microscopical examination of thin sections of the material (*a*) before testing; (*b*) after testing to the first evidence of softening at 1,225°; (*c*) after testing to 1,450° (turning point on the curves), and (*d*) after the second fall in the curve, at 1,600°, showed marked differences in structure. The results indicated that it was a question of a softening range of temperature rather than a softening point. Important points on the curves are at the commencement of softening and the point of rapid collapse. A relationship was also found between the surface area and the refractoriness and composition.

THE USES OF X-RAY SPECTROGRAPHY IN CERAMICS.—F. Rinne (*Ker. Rund.*, **33**, 427, 1925). The general principles of X-ray methods of investigating inorganic substances are outlined, the work of Lane, W. H., and W. L. Bragg, Schiebold, and Debye and Scherrer being reviewed. The application to ceramics is dealt with in a later article.

NEW PORCELAIN INSULATORS.—W. Cordes (*Ker. Rund.*, **33**, 113, 1925). Short descriptions, with sketches, are given of certain recent shapes in suspension insulators. (*cf.* Translation in *Cer. Ind.*, **4**, 460, 1925).

TERRA COTTA IN ARCHITECTURAL DESIGN.—F. S. Laurence (*J. Amer. Cer. Soc.*, **8**, 79, 1925). The artistic and decorative value of terra cotta is pointed out. The ceramic chemist should have a knowledge of what is required for architectural purposes.

ON THE STRENGTH OF HEAVY CLAY PRODUCTS.—J. H. Griffith (*J. Amer. Cer. Soc.*, **8**, 108, 1925). Simple laws for defining the strengths of heavy clay products are discussed, a permissible variation of $\pm 10\%$ being assumed. Simple equations are formulated to place the information in a simple form for architects and ceramists, to show the law of variation in terms of properly chosen variables, and to aid in appropriate selection of variables in devising future tests.

STONE DECAY AND THE PRESERVATION OF BUILDINGS.—A. P. Laurie (*J. Soc. Chem. Ind.*, **44**, 86T, 1925). In addition to the usual recognised

causes, (weather influences, etc.), the conversion of calcium carbonate into calcium sulphate is a potent factor in the decaying process in natural stones. Crystals of calcium sulphate form along certain layers or in pockets and thus break up the stone. This is the main cause of decay under modern conditions. The results of an investigation of the stone from different public buildings are presented.

PORTABLE EQUIPMENT FOR TRANSVERSE TESTS ON BRICKS.—H. D. Foster (*Claywr.*, **83**, 234, 1925). Portable apparatus is described which can easily be constructed, weighs 65 lbs., and can be operated by inexperienced men. Comparative tests showed that bricks failed in the portable equipment under an average stress of approximately 80% of that obtained by the standard method.

THE ACTION OF ARSENIC COMPOUNDS ON (GLASS) TANK BLOCKS.—D. J. McSwiney (*J. Amer. Cer. Soc.*, **8**, 307, 1925). An investigation of the cause of the excessive corrosion of glass tank blocks, observed when selenium is used as a decoloriser for soda-lime-flint glass, showed that the corrosive action is due to the arsenic used in conjunction with the selenium, and not to the latter substance itself. The degree of corrosion was not dependent upon the quantity of selenium added to the glass, but varied with the amount of arsenic used. The corrosive action is probably due to that portion of the arsenic compounds which separates out of solution as the glass cools.

IV.—MANAGEMENT, ORGANISATION, COSTING, ETC.: COMMERCIAL.

A MODERN BRICK PLANT.—J. T. Robson (*J. Amer. Cer. Soc.*, **8**, 159, 1925). A description of the Cleveland plant of the Ohio Clay Co. The bricks are fired in a tunnel kiln and the plant is laid out in an appropriate manner.

MODERN MECHANICAL EQUIPMENT OF AN ENAMEL WORKS.—A. Otremba (*Ker. Rund.*, **33**, 409, 1925). A plan showing the layout of a modern works, is given, together with illustrations of machinery and equipment.

CHECKING THE LIFE OF SAGGARS.—R. F. Sherword (*Ceramist*, **5**, 329, 1925). One of the best methods to determine the number of fires a saggar will withstand before it breaks down takes into account the number of saggars made and the number broken during a year. An example of the method in actual practice is as follows :—

a.	Total saggars on hand, Jan. 1st.	2,000
b.	,, ,, made during year	1,000
c.	,, ,, on hand, Dec. 31st.	1,500
d.	,, ,, broken during year	1,500
e.	No. of kilns fired during year	100
f.	Average No. of saggars broken per kiln	15
g.	Average No. of saggars placed in a kiln	300
h.	Percentage loss of life per saggar per fire	5%
i.	,, of total life of saggar	100%
j.	No. of fires per saggar	20

In the above list $d=(a+b)-c$; $f=d\div e$; $h=(f\div g)\times 100$; and $j=i\div h$. Considerable use may be made of item f ; it can readily be determined whether, at any given time, the breakage is running above or below the average for the past year. On plants where kilns are not all of the same size, the method is practically the same, though slightly more complicated

THE LABOUR COST IN COMMON BRICKS.—(*Brick* **66**, 120, 1925). The time required and the cost in labour for producing bricks by the soft

mud, stiff mud, and the dry-press methods are discussed in a general survey covering all departments of brick manufacture in America.

V.—GLASS: GENERAL.

DETERMINATION OF THE ANNEALING TEMPERATURE OF GLASSES BY A NON-OPTICAL METHOD.—H. Schönborn (*Ker. Rund.*, **33,** 397, 1925). The important equalisation temperatures of glasses, *i.e.*, the temperature at which the rate of stress equalisation has a definite value, bear a direct relation to those temperatures at which characteristic changes take place in certain physical properties, namely, the thermal expansion coefficient, the specific heat, and the electrical conductivity. Determination of these properties in relation to temperature, therefore, affords a means of determining the critical annealing temperatures of glasses.

REPRESENTATION OF THE COMPOSITION OF GLASSES AND GLAZES.—H. Hermann (*Sprech.*, **58,** 15, 1925). Devitrification phenomena provide data on the compounds contained in a glass. It is, therefore, natural to give the composition of a glass in silicates rather than in oxides, making allowance for the representation of possible associations and dissociations. The acid-alkali-lime (plate) glasses and the ordinary alumina (bottle) glasses can be represented by quoting the relative amounts of metasilicates, alumosilicates, alkali silicates, and free silica.

MANUFACTURE AND PROPERTIES OF DIFFUSIVE GLASS.—G. Schott (*Ker. Rund.*, **33,** 251, 1925). The various way of producing matt glass, *e.g.*, by sand blasting, etching, addition of opacifiers, etc., are dealt with. The phenomenon which occurs when rays of light strike a matt medium is considered.

"DAY LIGHT" CASE GLASS.—(*Ker. Rund.*, **33,** 300, 1925; *Sprech.*, **58,** 173, 1925). The so-called "daylight" glass, used for illumination purposes, consists of a bluish green ground glass cased with a dense opal glass. The composition (in kgs.) is:—ground glass—100 sand, 22 soda, 11 potash, 11 calcium hydroxide, 4 nitre, 3 borax, 0·45 copper oxide, 0·38 iron oxide, and 0·52 ferrous oxide; the case glass—100 sand, 20 soda, 8 potash, 6 calcium hydroxide, 13 cryolite, 2 nitre, 1 borax, and 0·12 manganese oxide. The ground glass is somewhat refractory and requires a high-temperature furnace.

THE ABSORPTION OF GASES BY MOLTEN SILICATES.—W. Estel (*Ker. Rund.*, **33,** 390, 1925). A good review of the literature of the subject is given.

SOFTENING AND ABSORPTION.—H. Schulz (*Ker. Rund.*, **33,** 395, 1925). A theoretical discussion of the subject.

MODERN ART GLASS.—(*Ker. Rund.*, **33,** 399, 1925). A review of the book by Pazaurck: "Kunstgläser der Gegenwart." 10 illustrations.

ACTION OF BARIUM IN GLASS.—(*Ker. Rund.*, **33,** 192, 1925; *cf.* Translation in *Glass Ind.*, **6,** 125, 1925). For better grades of table ware, barium oxide is used to replace sodium oxide, to give decreased solubility with consequent increased durability. Its chief advantage over limestone is that it facilitates melting and firing. Its principal use is to replace lead, its properties resembling those of the latter metal.

STRASS GLASS.—R. Schmidt (*Ker. Rund.*, **33,** 51, 1925). Strass glass (from the maker's name, Joseph Strasser, of Vienna, *ca.*, 1790), is a brilliant, colourless product, closely resembling the diamond, poor in alkalis and rich in lead (40-60% lead oxide), corresponding to the molecular formula: $6\ SiO_2.K_2O.2{\cdot}5PbO$. The literature on the subject, giving different batch mixtures, is reviewed.

POLLOPAS.—H. R. Schulz, R. Schmidt, and L. S. (*Ker. Rund.*, **33,** 142, 1925). The opinions of three glass experts on the new flexible glass are

presented (*cf.* TRANS., **23**, 106A, 1924).

GLASS TANK DESIGN.—J. A. Voorhies (*Glass*, **2**, 823, 1925). The problems dealt with include the determination of the size of regenerators, flue areas and the size of the stack.

NEW ELECTRICAL EQUIPMENT OF THE PITTSBURGH PLATE GLASS COMPANY.—A. L. Harrington (*Glass Ind.*, **6**, 93, 1925). A description is given of the use of slow-speed, vertically geared synchronous motors in grinding and polishing plate glass.

BOTTLE MAKING IN INDO-CHINA.—D. Robertson (*Glass Ind.*, **6**, 115, 1925). An account of glass manufacturing conditions in the Far East.

THE CAUSES OF COOLING-CRACKS (CRIZZLES) AND WRINKLES (WAVES) IN PRESSED GLASS.—E. Zschimmer, K. Hesse, and K. Meures (*Sprech.*, **58**, 185, 1925 ; *cf.*, Translation in *Glass Ind.*, **6**, 120, 1925). The explanation is based on the assumption that a leather-hard skin forms on molten glass immediately upon exposure, and that this skin cracks when pressure is applied, in forming an object of larger surface area than the original gather, or folds when compressed into smaller area.

DEFECTS IN GLASS. II.—C. J. Peddle (*Glass*, **2**, 652, 1925). The cause and prevention of bubbles, seeds, etc., in glass are discussed.

DEVELOPMENTS IN THE GLASS INDUSTRY.—B. Schieldrop (*Glass*, **2**, 665, 1925). The greatest progress is shown in the plate glass industry. Patents indicate that much attention is being devoted to the forming department, but less to the melting process.

THE GLASS INDUSTRY.—(*J. Soc. Chem. Ind.*, **44**, 650, 1925). A brief survey is given of the history and development of the glass industry.

GLASS HOUSE EXPERIENCES.—R. R. Shively (*Ceramist*, **1**, 45, 1924). Details are supplied of eight problems, and their solutions, encountered over 11 years of consulting work.

DEFECTS IN GLASS—DEVITRIFICATION. III.—C. J. Peddle (*Glass*, **2**, 816, 1925). The influence of stabilising oxides upon devitrification is discussed.

ELECTROLYSIS OF SODA-LIME GLASS. I.—EVOLUTION OF GAS AND ITS RELATION TO SORPTION AND CONDUCTIVITY.—J. W. Rebbeck and J. B. Ferguson (*J. Amer. Chem. Soc.*, **46**, 1991. 1924). Glass bulbs filled with mercury were immersed in dilute sodium hydroxide solution, and an electric current passed through. With a mercury cathode, gases consisting mainly of hydrogen mixed with a little oxygen were evolved. Heating the tubes in a vacuum for long periods at 350° prevented evolution of gas, but this property was regained on exposing the tubes to water or water vapour. No gas is evolved with a mercury anode. The gas evolution is due to the electrolysis of sodium hydroxide formed by the action of sodium on sorbed water. The resistance of the glass is not affected by sorption of water, but it is increased considerably by the heating process. The glass contained 71·08% SiO_2, 18·85% Na_2O, 6·22% CaO, 3·38% MgO, plus traces of Al_2O_3, Fe_2O_3, and ZnO.

THE ELECTROLYSIS OF SODA-LIME GLASS. II.—J. W. Rebbeck, M. J. Mulligan, and J. B. Ferguson (*J. Amer. Cer. Soc.*, **8**, 329, 1925). At low temperatures (46°-94°) no deviations from Ohm's law were detected with glass, the composition of which had not been altered by electrolysis. The relation between the time of annealing and the electrical resistance, and between the temp. coefficients of the resistances of annealed and unannealed glasses were investigated, the results being shown by curves. The nature of the change produced in glass by correct heat treatment was studied by electrical migration experiments, using silver nitrate. The marked increase in resistance was found to be due mainly to a decrease in the speed of the sodium ions and to a slight change in their number. The resistance also

depends upon the direction of the current; with murcury cathode the apparent resistance changes little, whereas with mercury anode, it increases continuously as the electrolysis proceeds, and the rate of change of resistance increases with time. The results of experiments hitherto obtained point to a type of polarisation as an explanation of this phenomenon rather than to the theory of a highly resistant layer.

ANALYSIS OF RECENT MEASUREMENTS OF THE VISCOSITY OF GLASSES.—G. S. Fulcher (*J. Amer. Cer. Soc.*, **8**, 339, 1925). The data supplied by two recent investigations (S. English, *J. Soc. Glass Tech.*, **7**, 25, 1923, and **8**, 205, 1925, and E. W. Washburn, G. R. Shelton, and E. E. Libman, Univ. Illinois Eng. Exp. Station, *Bull.*, **140**, 1924), are subjected to a graphical analysis in order to compare and correlate the results. The absolute values of $\log_{10}$ viscosity (η) given by Washburn *et al.* are higher to the extent of 0·6 than those obtained by English. Allowing for this correction, the isothermal curves of $\log_{10} \eta$ as a function of soda content are smooth up to 50% of Na_2O. As a function of temperature (T), the observations are all represented by the equation: $\log_{10} \eta = -A + B \times 10^3 / (T - T_0)$, in which the three constants A, B, and T_0 vary regularly with the composition. Curves showing as a function of temp. the change in $\log_{10} \eta$ produced by molecular substitution of lime, magnesia, and alumina for soda show sharp bends between 840° and 1,050°. This point is called the aggregation temperature (T_a). The aggregation temperatures coincide fairly closely with devitrification temperatures, but the two are quite distinct; the former occur at a definite point and reach a limit which is a function of the lime content, whereas the latter vary with time. At T_a, the change in $\log_{10} \eta$ per cent. substituted shows a minimum value. 0·03-0·06 for lime, 0·12 for magnesium, 0·07 for alumina. More complex curves are obtained on substituting boric oxide for silica in soda—boric oxide—silica glasses.

THE PRINCIPLES AND PRACTICE OF ANNEALING GLASSWARE.—S. R. Scholes (*Glass Ind.*, **6**, 8, 1925). The modern automatic muffle lehr serves the additional purpose of acting as a conveyor between factory and sorting room. Annealing proper is accomplished in the first 20 feet of the average lehrs, the remainder of its length serving simply as a storage and conveyor. This portion need not be built solidly of bricks. The control of the temperature gradient is of vital importance. Internal strains can readily be discovered by examining the glass in polarised light.

ENGLISH "PYREX" GLASSWARE.—G. E. Stephenson (*J. Soc. Chem. Ind.*, **44**, 299, 1925). The manufacture of "pyrex" glass was introduced into England, from America, in 1923. The process by which it is made (at Sunderland) is described. Both the tank furnace and annealing ovens are oil-fired. The advantages of "pyrex" over Jena ware are pointed out.

Patents

IMPROVEMENTS IN GLASS MELTING FURNACES.—The United Glass Bottle Manufacturers Ltd. and T. C. Moorshead (*Brit. Pat.*, 227,939, 27 Oct., 1923). To prevent the formation of dormant glass in the corners of tank furnaces, the sides of the bridge wall separating the working from the melting compartment are inclined or curved so as to avoid right-angled corners in the compartments. The latter are of oval, torpedo, hexagonal, octagonal or similar formation. The bridge wall is formed of two sections projecting into the furnace, leaving at the centre a gap which is partially closed by a floating ring of refractory clay.

ROLLING GLASS.—Pilkington Bros. Ltd. and E. B. le Mare (*Engl. Pat.*, 228,627, 7 Nov., 1923). A continuous strip of glass is produced by passing molten glass from a tank on to a moving table or roller. A pool is formed, which is carried into the pass of the rolling apparatus. The edges of the pool are protected from excessive cooling by side walls.

FORMING SILICA-GLASS ARTICLES.—British Thomson-Houston Co., Ltd. (*Engl. Pat.*, 222,119, 12, Sept., 1924). Fused silica tubes are formed by heating the end of a silica rod until it is plastic, mechanically perforating a portion of the plastic rod along its longitudinal axis, and then applying gaseous pressure internally to expand the rod to tubular form.

FROSTING GLASS.—British Thomson-Houston Co. (*Engl. Pat.* 228,907, 4/2/25). Electric lamp bulbs are treated with an agent having a solvent action, *e.g.* ammonium, potassium or sodium bi-fluoxide solution, the object being to strengthen the bulb.

TOUGHENING GLASS.—Schott & Gen, and K. Hirsch (*Engl. Pat.*, 223,353, 21. Aug., 1923). Glass articles are submitted, while hot, to the chilling action of air blasts, or by immersion in a suitable liquid. The cubical coefficient of expansion if the glass must not exceed 200×10^{-7}.

FUSED SILICA; FORMING SILICA-GLASS ARTICLES.—Quartz et Silice (*Engl. Pat.*, 224,163, 5 May, 1924). Silica is melted in actual contact with a mould of refractory and conducting material which is heated by high-frequency electric currents. A device for making insulators is shown.

FORMING SILICA-GLASS ARTICLES.—Quartz et Silice (*Engl. Pat.*, 224,164, 5 May, 1924). Silica is melted in a crucible, as described in *Spec.*, 224,163, the plastic silica being expelled from the crucible either by pressure or by drawing. The mass is then shaped by pressure or other suitable means.

DELIVERING MOLTEN GLASS FROM FURNACES.—J. T. Wood (*Engl. Pat.*, 229,804, 28/12/23). A timing device is described, which is intended for use with glass feeding mechanism and which adjusts the various operations of such mechanism relatively to one another.

FUSIBLE GLASSES AND ENAMELS.—General Electric Co., Assees. of Patent Treuhand G s. (*Engl. Pat.*, 233,295, 14/10/24). The glasses and enamels described in the parent Specification (No. 223,837, *cf.* TRANS. **23**, 107A, 1924), are made non-resistant to chemical action by increasing the silica content, the boric acid content being decreased at the same time in order to maintain the low fusing-point. The alkaline or alkaline earth oxides are replaced by the oxides of zinc, magnesium, calcium, borium, or lithium, which reduce the coefficient of expansion. The molecular composition is then as follows:—PbO, 1; ZnO (or Al_2O_3, CaO, MgO, BaO), 0·04-0·15; SiO_2, 0·3–0·6; Li_2O (or Na_2O, K_2O), 0·04–0·15; B_2O_3, 0·23–0·35; colouring oxide, 0–0·1. To render the enamel opaque, cryolite, or calcium or other fluorides may be fused with the material.

FORMING SILICA GLASS ARTICLES.—British Thomson-Houston Co. (*Engl. Pat.*, 230,499, 9/3/25). Tubes or rods are produced from silica by passing an electric current through a carbon rod, surrounded by silica, the plastic silica being then drawn from a region near the heating rod.

PRESSING GLASS.—F. Rosengarth (*Engl. Pat.*, 230,846, 13/3/25). A press for moulding cells or cases for accumulators, etc., has a fixed bottom and sides which can be moved inward to press the glass toward a core.

FORMING GLASS THREADS.—K. Haddon, for Corning Glass Works (*Engl. Pat.*, 233,136, 3/5/24). A number of drawn strands of molten glass are wound on a drum in a helical winding, the adjacent turns being separate from each other.

VI.—CEMENT, CONCRETE, MORTARS, ETC.

THE MECHANISM OF SETTING OF CALCIUM SULPHATE CEMENTS.—C. L. Haddon (*Trans. Faraday Soc.*, **20**, 337, 1924). Theories which have previously been put forward are critically examined. An explanation is offered to account for the fundamental differences in the hydration processes between plaster of Paris, flooring plaster and anhydrite, the varying effect of catalysts being thereby explained. Further evidence in

support of Desch's theory of crystal thrust is advanced. The similarity between the coherence of calcium sulphate cements and that of metals is pointed out.

CEMENT MANUFACTURE AND ITS POSSIBILITIES IN THE CROWN COLONIES AND PROTECTORATES. III.—(*Bull. Imp. Inst.*, **23**, 32, 1925). The possibilities of cement manufacture in the British West Indies and other colonies in the Western Hemisphere, and in the island colonies and protectorates of the Pacific are discussed.

THE BEHAVIOUR OF METAL OXIDES IN GROUND-COAT ENAMELS.—L. Vielhaber (*Ker. Rund.*, **33**, 53, 1925).

RAPID HARDENING PORTLAND CEMENT AND CONCRETE.—A. Gessner (*Tonind. Ztg.*, **49**, 223, 1925). A general report on the tests carried out by the German Bureau for Testing Materials in Czecho-Slovakia.

SOLUBLE SILICA AS A MEANS OF WORKS CONTROL.—O. Frey (*Tonind. Ztg.*, **49**, 337, 1925). A method is described by which the determination of the soluble silica, which plays an important part in the hardening process of cement, may be utilised to control the quality of the output.

WATER FOR CONCRETE MIXING.—D. A. Abrams (*Chem. Tr. J.*, **76**, 295, 1925). Some 6,000 tests were made with clean, porable waters, bog water, sea and alkali water, mine and mineral water, sewage and industrial waste waters and salt solutions. Most of the impure waters gave good results. Neither odours nor colour gave indication of the suitability of waters. Acid waters, and water containing over 5% common salt gave strengths below the 85% limit (compared with the corresponding fresh water concrete). The important factor was found to be the *quantity* of impurities present in the water.

GRANULATING AND DRYING BLAST FURNACE SLAG.—Various (*Stahl Eis.*, **45**, 529, 1925). An illustrated account is given of the methods adopted on five different plants.

OXYCHLORIDE CEMENTS AND ARTIFICIAL WOODS.—"Deleta" (*Chem. Tr. J.*, **76**, 635, 1925). The method of making "xylolith," its properties, uses, etc., are described. A review of the patent literature is appended.

Patents

HYDRAULIC BITUMINOUS CEMENT IN POWDER FORM AND PROCESS FOR MAKING IT.—G. D. Coletta (*Engl. Pat.*, 227,966, 10 Sept., 1924). Portland cement, lime, and an inert hardening substance are incorporated with asphaltic bitumen in a melted state ; the mixture is cooled, crushed, and then ground with an equal weight of powdered Portland cement. The final product consists of 15-20% of asphaltic bitumen, 75-80% of Portland cement, 3-4% of lime, and 1-2% of an inert hardening substance (silicious sand).

ROTARY FURNACE FOR FUSED CEMENT.—Soc. Anon. des Ciments Français, and Bureau d'Organisation Economique (*Engl. Pat.*, 232,155, 16/5/24). The materials are fed into a zone maintained at a temp. below 1,000° by external cooling, then passed to a zone at 1,600-1,700°, and discharged in a molten state at a temp. above 1,500°.

MANUFACTURE OF ARTIFICIAL STONE.—E. C. K. Marks, Assee. for G. Polysius (*Engl. Pat.*, 234,302, 24/6/24). More or less finely ground slag, of any kind, is mixed with unburnt gypsum or anhydrite, the mixture being pressed to the desired shape. The slag may be ground or unground, or a mixture of both, dry or moist, and the unground slag may be replaced by sand. The gypsum also may be ground or unground. Alkaline substances such as soda, calcium oxide, may be added.

PROCESS AND APPARATUS FOR THE MANUFACTURE OF STONE-LIKE MATERIAL.—F. Euwecke (*U.S. Pat.*, 1,518,842, 9. Dec., 1924). A mixture of 5% by weight of calcium hydroxide and 95% granulated silicious

slag is burned and delivered at about 188°, moulded at a temperature of about 93°, the moulded material being subjected to the action of carbon dioxide for 3 hours at a pressure of approximately 140 lb. per sq. in. and a temperature of 21°. The calcium hydroxide and carbon dioxide are obtained by burning limestone in the first stages of the process.

ALUMINOUS CEMENT.—L. G. Patrouilleau, and Alumina et Dérivés (*Engl. Pat.*, 232,898, 19/12/24). Suitable sulphur compounds are added to the raw materials for making aluminous cement, either before, during, or after charging into the furnace, in order to prevent the formation of silicates.

ALUMINOUS CEMENTS.—U. B. Voisin, Assee. of E. M. Roche (*Engl. Pat.*, 233,698, 6/5/24). A mixture of 50 pts. by volume of medium hydraulic lime or limestone and 50 pts. of bauxite are ground, briquetted and burnt at 1,200-1,500° for 12 hours. After grinding, the hard, black clinker sets in 2-3 hours. By employing fat lime and burning more slowly, a cement is obtained which sets almost immediately.

CEMENT TILES.—A. Brune (*Engl. Pat.*, 233 819, 3/3/24). Cement tiles, with a facing of cement and colour, are hardened by treatment with moisture at 20-40° at ordinary pressure and subsequently with steam at 9 atm. for 6-8 hours.

METALLIC OXIDE CEMENTS.—E. C. R. Marks (Economy Fuse & Manufacturing Co.). (*Engl. Pat.*, 233,907, 16/6/24). An aluminate of an alkaline metal (calcium aluminate) is used as primary binding substance and the setting liquid contains phosphoric acid. From 2 to 10% of aluminate may be present, and the setting liquid may contain a phosphate. Five sample mixtures are given.

VII.—CHEMICAL AND ANALYTICAL PROCESSES.

THE ANALYSIS OF COMMERCIAL SODA.—E. Schönach (*Emaillew. Ind.*, **1**, 95, 1925).

THE CONSTITUTION OF THE SILICATES.—Geyger (*Emaillew. Ind.*, **1**, 13, 1925).

ISOLATION AND QUANTITATIVE DETERMINATION OF COBALT.—Geyger (*Emaillew. Ind.*, **1**, 14, 1925).

THE ANALYSIS OF QUARTZ.—E. Schöneich (*Emaillew. Ind.*, **1**, 25, 1925).

THE INTERACTION OF SODIUM CHLORIDE AND ALUMINA.—F. H. Clews (*J. Chem. Soc.*, **127**, 735, 1925). The following reactions were confirmed: (*a*) $4x\ NaCl+yAl_2O_3+xO_2=2xNa_2O,\ yAl_2O_3+2xCl_2$; (*b*) $2xNaCl+yAl_2O_3+xH_2O=xNa_2O,\ yAl_2O_3+2xHCl$; (*c*) $4\ HCl+O_2=2H_2O+2Cl_2$. Reaction (*b*) is reversible at about 1,000°. The formation of aluminium chloride was not observed in the presence of water. Reaction (*b*) predominates, and the chlorine produced is attributed to (*c*) rather than to (*a*), since it is dependent upon the supply of air and water. Above 1,000° the reaction of a given quantity of NaCl with Al_2O_3 is virtually complete. The stability of sod. aluminate with reference to HCl decreases rapidly at 1,045° when the molecular ratio Al_2O_3/Na_2O is less than 10 : 1, and at 830° when less than 12 : 1. Excess of Al_2O_3 rather than of water is essential for complete reaction of NaCl with Al_2O_3 in the presence of water.

COMPARISON OF METHODS OF ANALYSIS OF GYPSUM.—P. P. Budnikoff (*J. Amer. Cer. Soc.*, **7**, 817, 1924). An attempt was made to develop a standard method of analysis, the various methods proposed being subjected to experimental tests. A reliable and rapid analysis of gypsum for the determination of $CaSO_4$, for industrial purposes, was obtained by combining Andrew's and the $KMnO_4$ titration methods.

EXPERIENCES WITH GLASS FILTERS IN ANALYTICAL CHEMISTRY.—G. F. Hüttig and M. Nette (*Keram. Rund.*, **33**, 99, 1925). The authors give an account of their experiences with filters of porous glass in carrying out qualitative analyses. A few notes are added on methods of conducting quantitative analyses.

X-RAY INVESTIGATION OF CRYSTALLINE SUBSTANCES, AND ITS CHEMICAL APPLICATIONS.—G. R. Levi (*Giorn. Chim.*, **7**, 78, 1925).

VIII.—HISTORICAL, EDUCATIONAL, INSTITUTIONS, ETC.

NEW WESTERWALD STONEWARE.—Berdel (*Ker. Rund.*, **33**, 114, 1925). The technique of hand-cut intaglio ware and decorative work in bas-reliefs has been revived. Illustrations of ware are given.

TURKISH STONEWARE, OLD AND NEW.—Berdel (*Ker. Rund.*, **33**, 122, 1925).

ACCOUNT BOOKS OF ROMAN POTTERS.—C. Blümlein (*Ker. Rund.*, **33**, 172, 1925). In a book by F. Hermet ("Les Graffites de la Granfesenque," Rodez, 1923), details are given of inscriptions on fragments of Roman pottery. The inscriptions are found chiefly on the bottoms of broken dishes and are in 3 columns, the first giving usually the name of the workman, the second the name or type of the article, and the third, the number of articles made by the workman. (4 illustrations).

THE CERAMIC INDUSTRY OF CASTELLI (TERAMO).—H. Herda (*Ker. Rund.*, **33**, 203, 1925).

ENGLISH POTTERY.—B. Backham (*Pot. Gaz.*, **50**, 442, 1925). Report of a lecture delivered at the Victoria and Albert Museum.

THE LATER CERAMIC WARES OF CHINA.—K. L. Hobson (*Pot. Glass Rec.*, **7**, 150, 1925).

THE FRENCH PORCELAIN INDUSTRY.—(*Sprech.*, **58**, 357, 1925). A short historical sketch, with statistics, is given.

THE POTTERY COURSE AT THE PENNSYLVANIA MUSEUM SCHOOL OF INDUSTRIAL ART.—E. de F. Curtis (*J. Amer. Cer. Soc.*, **8**, 138, 1925). The course is designed to familiarise students with all decorative processes. The equipment is of the simplest. A small kiln, fired by kerosene, is described. Formulæ used at the School are given.

THE REFRACTORY INDUSTRY OF NEW JERSEY.—F. B. Allen (*Ceramist*, **1**, 21, 1925). A historical sketch of the development of the fire-brick industry is given.

Review.

A Text Book of Glass Technology.

By F. W. Hodkin and A. Cousen. (Constable & Co., Ltd., London, pp. 550. Price £2 2s. 0d.)

In a foreword to this excellently printed and illustrated volume, Prof. W. E. S. Turner states that ".....the success of the glass industry must depend in an increasing degree on the thoroughness of the technical knowledge of its leaders, and this introductory text-book is, I believe, a definite and helpful contribution to this end....." The authors' preface suggests the industrial field of their effort :".....to masters who desire factories run on sound up-to-date principles, and to workmen who wish to know something of the theory involved in the processes in which they are day by day engaged. .....The keynote of the volume has been simplicity ; theories at present in debate have been treated only lightly, and the more complex side of them passed over.....". In attempting to fulfil this ideal, the authors have produced, within the relatively limited scope of 550 pages, a welcome addition to an extremely important but hitherto almost neglected branch of silicate technology, so far as book publication in this country is concerned.

The chapter and general arrangement of the book seems good ; a short historical introduction leads to separate considerations of the physical, optical and other properties of glasses. Chapters VII. to XII. deal with raw materials, batch mixing, storing and drying, and glass-making calculations. Combustion, fuels, the thermochemistry and valuation of fuels, producer gas and gas-producers are treated in a manner which might possibly be more modernised and less copiously illustrated with the stereotyped drawing-office productions. Incidently, the separate chapter on pyrometry contains no mention of the useful disappearing-filament type of pyrometer.

The worthy subject of refractory materials, including the manufacture of glass-house pots and blocks, is honoured to the extent of some 57 pages ; seven succeeding chapters deal with direct and semi-direct fired furnaces, gas-fired and oil-fired regenerative and recuperative installations, annealing furnaces, etc. The last 130 pages of the volume include very readable and interesting descriptions of the almost miraculous devices used in the large scale manipulation and shaping of glass.

It may be appreciated from this résumé that the authors could, justifiably, have included the term "comprehensive" in the title.

The book is comparatively free from such detail errors as may perhaps, be excused in the first edition of almost any novel enterprise. Nevertheless, a few incongruencies seem to merit special attention. Thus, the *definite* melting points for the felspars tabulated on p. 157 are hardly in agreement with the well-established Day and Allen melting curves shown on p. 163 ; the section on magnesia has no reference to the Austrian deposits ; and the idea is conveyed (p. 116), that fluxing is purely a chemical phenomenon. We might perhaps regard the remark on p. 107 : ".....the pure material (zinc oxide) dissolves completely in acid without liberation of bubbles of carbon-dioxide.....," as a technical hint and not as a chemical redundancy. Again, there is a distinct lack of agreement between the definite statement on p. 65 : ".....no sand is a first-rate glass sand if it contains less than 99% SiO_2" and the analyses of the "most widely used" glass-sands, including *Aylesbury* and other British, and Belgian sands, tabulated on p. 84. Such errors will, no doubt, be eliminated as soon as the opportunity arises.

In the reviewer's opinion, however, faulty space distribution in a few sections of the book calls for the most criticism. It seems a pity that the fundamental work of English (and of Field) on viscosity-temperature-composition relations of glasses could not have been incorporated in the text,

instead of being relegated to a ten line appendix at the end of the section on viscosity.

Similarly, the allocation of space in the chapters dealing with refractories appears to be somewhat at fault. ".....It is at present impossible to forecast the softening point of a clay by a consideration of its composition ....." say the authors ; yet, while they devote two and a half pages to this problem, "one of the most important physical properties of clays when in commercial use, the refractoriness under load," is dismissed in a single page, half of which is filled with a tabulation of "crushing strengths," now known to have little, if any, practical importance.

Although the glass industry is notorious for low thermal efficiencies, it is rather astonishing to find the consideration of thermal conductivity dismissed in four sentences. Again, a very full and splendidly illustrated description is given of the manufacture of glass-pots by hand, but the more scientific and less easily understood process of casting receives a rather meagre treatment.

Yet the undoubted value of the book, considered as a whole, overshadows its minor faults, and it is possible to recommend this volume with confidence to all who are interested in silicate technology, and to many who are not.

It constitutes a commendable effort and one which will gain for the authors the gratitude of technologists in general and of glass manufacturers and workers in particulars.

A. J. Dale

Abstracts.

I.—RAW MATERIALS.

OCCURRENCE, PREPARATION, ETC.

OPERATING THE ENGLISH CLAY PIT.—W. Barnes (*Brick*, **66**, 584, 1925). Details are given relating to the methods of getting the clay, type of equipment used, and stripping the overburden.

THE ZETTLITZ KAOLIN WORKS.—H. Köbbinghoff (*Ker. Rund.*, **33**, 541, 1925). The methods of procuring, washing, and despatching the china clay are illustrated and described.

POSSIBLE PRODUCTION OF TITANIUM WHITE FROM CANADIAN SOURCES.—H. A. Leverin (*Can. Chem. Met.*, **9**, 198, 1925). The possibility of producing titanium white economically from Canadian deposits of ilmenite is discussed.

GRAPHITE, AND ITS INDUSTRIAL APPLICATIONS.—L. Maugé (*Cer. Verr.*, **45**, 353, 1925). An account of the sources from which graphite is obtained is followed by a description of the method of preparing graphite crucibles, etc.

PURIFYING AND UTILIZING WASTE CERAMIC RAW MATERIALS.—Jirokichi Kumazawa (*J. Jap. Cer. Assoc.*, **33**, No. 386, 41, 1925). The purification of ceramic raw materials by bleaching them with chlorine at high temperatures is useless, because they are deprived of plasticity. The bleaching of bodies in the biscuit firing was therefore tried. The following table shows the temperature ranges, in which typical Japanese raw materials produce biscuit bodies with suitable strength and pososity :—

Gairome, Kibushi, Korean kaolin and bodies made of them	900°-1050° ;
Aizu-ware (liparite body, contg. small amt. of lime) ..	900°- 950° ;
Tobe-, Arita- and Kutani-wares (liparite bodies) ..	1050° ;
Amakusa stone (semi-decomposed liparite)	1050°-1100°.

A small coal-fired muffle kiln, 2 ft. high, 1·5 ft. wide and 1·8ft. long, with two shelves, was used, chlorine being introduced through a hole at the centre of the door and drawn through two lower holes in it. Biscuit firing at 940° was not satisfactory, though it was better than that at 800°. Firing at 1,000°, the gas being admitted for six hrs., gave a better result. S. Kondo.

ACTION OF ELECTROLYTES ON CLAYS. Seiji Kondo (*J. Soc. Chem. Ind. Japan*, No. 322, 1315, 1924). For preliminary experiments on the adsorption of malachite green by various clays, a chemically pure HCl-salt of the tetramethyl diparaamido-triphenyl carbinol was used. The amounts of the dye adsorbed by 1 g. of 25 typical high-grade clays are compared with their physical properties which are closely connected with plasticity. The plasticity of 9 clays, as measured by the adsorption of the dye, did not agree with the facts. The author succeeded in determining the dye by titrating with $KMnO_4$, or, better, with picric acid, the results being far more accurate than those obtained by the usual colorimetric method. The results of experiments with 5 high-grade clays show that the Freundlich formula does not hold for the adsorption of dye by clays. The electrical conductivity of the dye solutions obtained in the preceding experiments and that of the pure dye sometimes of various concentrations were measured. The results show that the conductivity of the pure malachite green solution is not materially affected by treating with a clay. The phenomenon is explained as follows : $C_{23}H_{25}N_2Cl = C_{23}H_{25}H_2^+ + Cl^-$; $M + C_{23}H_{25}N_2^+ = M^+ + C_{23}H_{25}N_2$; where M^+ is an equiv. of cation which has been combined with clay. Thus, an equivalent amount of cation is set free from the clay and accordingly no remarkable change in conductivity occurs. The Cl content of the dye solution is only slightly affected by the adsorption. The effect of the concentration of the dye solution on the adsorption is slight, provided that the ratio of the dye

to the clay remains constant. K. assumes that the adsorption is a chemical reaction. Assuming that the clay has only potassium kaolinate, the molecular formula of which is taken to be KA, the reaction may be expressed by :— $KA + C_{23}H_{25}N_2Cl = KCl + C_{23}H_{25}N_2A$. If the molecular concentrations of these substances are $m_1 m_2, m_3$ and m_4 with degrees of ionization, $d_1 d_2 d_3$ and d_4 at equilibrium, we have the relation $m_1 d_1 . m_2 d_2 = m_3 d_3 . m_4 d_4$. Since kaolinates are assumed only sparingly soluble in water, $m_1 m_4$, d, and d_4 may be assumed as constant. Thus the equation becomes $m_2 d_2 = m_3 d_3$, which clearly explains the fact. The surface tension of the dye solutions is affected by the adsorption, but no useful conclusion is deduced. The adsorption of the dye by English china clay and Korean kaolin, which had been fired at 110-1,410° was studied. Results : (1) Korean kaolin fired at 1,300° has a strong adsorptive power, which corresponds to 46·1 per cent. of that of the kaolin dried at 110° ; (2) The colour of the resulting sample fades rapidly as the firing temperature rises, and those fired at 1,200° are only slightly green ; (3) Remarkable changes in adsorption occur at 500° and 1,200°, and a less marked one at 800°-1,000°, where thermal changes were assumed to take place by Mellor and others ; (4) Fired kaolins rehydrate in a moist atmosphere ; (5) The fired kaolins do not adsorb Cl from the dye solutions. The results of the experiments with methyl violet 2B and the clays show that it can be used for measuring their plasticity ; but the fact that the dye-clay suspension clarifies very slowly is a serious defect of the dye. The adsorption of KOH, $Ba(OH)_2$, K_2CO_3, KCl, $BaCl_2$, Fe_2Cl_6, $Fe_2(SO_4)_3$, $AgNO_3$, $MnSO_4$ and HCl by Korean kaolin was studied. Varying amounts of each electrolyte were added to 10 g. of Korean kaolin, one of the purest kaolins in the world, and 300 cc. of water. The mixtures were agitated for several hrs. After settling, the clarified solutions were analysed for each electrolyte, SiO_2, Al_2O_3, Fe_2O_3, CaO,MgO and alkalies. The conclusions are: (1)clay adsorbs inorganic elctrolytes, just as it does dyes, and adsorbs considerable amounts of their cations completely, leaving no trace in the solutions, as shown in the following table :—

	Amts. of the compds. which 1 g. of the kaolin can adsorb in milli-equiv.	Amts. of the compds. which 1 g. of the kaolin can adsorb completely in milli-equiv.
$C_{23}H_{25}N_2Cl$	0·566	0·036
KOH	$0·634 + x$	0·027
$Ba(OH)_2$	$0·514 + x$	0·153
K_2CO_3	$0·432 + x$	0·000
KCl	0·107	—
$BaCl_2$	0·153	0·052
Fe_2Cl_6	0·287	0·123
$Fe_2(SO_4)_3$	0·374	0·124
$AgNO_3$	0·178	0·027
$MnSO_4$	0·205	0·054
HCl	$0·357 + x$	0·108

(2) Only cations take part in the adsorption ; (3) The adsorption is chiefly affected by the nature of the anion and the solubility of the resulting kaolinate in water. The adsorption of electrolytes with the same cation decreases as the acidity of the anion increases, whilst the adsorption of electrolytes with the same anion increases as the solubility of the resulting kaolinate decreases ; (4) Cations of the electrolytes displace the equivalent amount of cations ; the peculiarly rising slope of the adsorption curves for some electrolytes is probably due to the presence of the kaolinates of several cations on the surface of the clay ; (5) The general tendency of the adsorption equilibrium is such that acid reacts first with kaolinates, while alkali reacts first with kaolinic acid ; Neutral salt merely displaces the cations of kaolinates. The equilibrium is not materially affected by dilution ; this is explained by means of the law of mass-action. The plasticity of clays was measured by means of manganous sulphate. The amounts of manganous sulphate which were adsorbed by 10 g. of each of 16 clays were compared with their air shrinkage, surface factor, tensile strength, binding power and plasticity-water. More satisfactory results were obtained than with the dye. Moreover, the salt is obtainable

in a very pure state and can be estimated more accurately than the dye.

S. KONDO.

INCREASING THE PLASTICITY OF FULLER'S EARTH.—The Institute of Physics and Chemistry (*Jap. Pat.*, 2,236 (1924), 17/11/24). In the process of working up Fuller's earth or a mixture of Fuller's earth and other minerals with water, a small amount of oxalic acid or an acid oxalate is added. The acid or its salts deflocculate the earth and increase its plasticity.

S. KONDO.

BLEACHING CLAY AND ROCK POWDER.—A. Matsubara (*Jap. Pat.*, 62,418, 17/2/25). A low-grade clay is mixed with 2-5*N* H_2SO_4 in a tank fitted with a stirrer, hydrogen sulphide being passed through the solution which is heated to, and maintained at 50°-70°. Ferric compounds in the clay are reduced by the gas and dissolved by the acid. In about one-and-a-half hours, the iron, together with the greater part of the manganese and chromium, will be dissolved. Then the product is elutriated to get rid of undecomposed coloured minerals and sands. Semi-decomposed liparite, pegmatite, quartz, talc, agalmatolite, barium sulphate, etc., may be treated in a similar manner.

J. KONDO.

PHYSICAL AND CHEMICAL PROPERTIES, TESTING, ETC.

AN X-RAY STUDY OF CYANITE AND ANDALUSITE.—J. T. Norton (*J. Amer. Cer. Soc.*, **8**, 636, 1925). Natural, raw cyanite and andalusite have different atomic structures, both the positions and the relative intensities of the lines in the diffraction patterns showing distinct variations. After having been heated to about 1,450° and about 1,600° respectively, the two compounds exhibit the diffraction pattern of artificial sillimanite.

DIFFERENTIATION BETWEEN MULLITE AND SILLIMANITE BY THEIR X-RAY DIFFRACTION PATTERNS.—L. Navias and W. P. Davey (*J. Amer. Cer. Soc.*, **8**, 640, 1925). X-ray diffraction patterns were obtained for natural sillimanite, mullite (prepared by fusing alumina and silica), and calcined china clays and ball clays. The patterns of two substances were taken, one above the other, on the same film, the lower one in each case being that of mullite, so that direct comparison was possible. In the patterns for sillimanite and mullite distinct differences in the positions of lines in the region of 2·12A to 1·70A were apparent. Examination of diffraction patterns previously obtained (TRANS., **24**, 28A, 1925) for calcined china clays and ball clays showed definitely that the crystalline phase of fired clays is mullite. The specimens were prepared by the "powder method." Sillimanite and mullite showed entirely different characteristics on grinding. When ground and sieved to give a maximum particle size of 0·06 mm. the lines of the sillimanite pattern were smooth, whereas those of the mullite pattern were scratchy in appearance, indicating that the mullite fragments had "packed" to form lumps. The negative results obtained by other investigators are accounted for by this packing tendency. Mullite ground to an average particle size of 0·002 mm. and annealed for 2 hrs. at 900°-1,000°, gave lines as smooth as those of sillimanite.

CHEMICAL AND PHYSICAL PROPERTIES OF FIRECLAYS FROM VARIOUS (AMERICAN) PRODUCING DISTRICTS.—M. C. Booze (*J. Amer. Cer. Soc.*, **8**, 655, 1925). A number of plastic and non-plastic clays from various American sources were submitted to the standard tests of the Amer. Cer. Soc.. for chemical composition, fusion point, drying and firing shrinkage, and fired porosity. The results are briefly discussed.

PROGRESS REPORT ON THE USE OF ANDALUSITE AS A REFRACTORY.—R. Twells, jr. (*J. Amer. Cer. Soc.*, **8**, 485, 1925). A deposit of andalusite, which contains small quantities of corundum and pyrophyllite, is being used in the development of andalusite as a refractory. Up to its inversion point, andalusite retains all its optical properties except for the formation of small glass-like inclusions, apparently due to impurities. During inversion, it does not lose its original outward form, a most important quality. The

presence of a small amount of siliecous glass may be an advantage, owing to its bonding strength and low coefficient of expansion. For very high temperatures, diaspore or bauxite may be added to the andalusite in amounts sufficient to give the mullite ($3Al_2O_3.2SiO_2$) ratio. *Under-load strength.* A raw andalusite (100%) brick gave a deformation of 0·38% in the standard test, as compared with 4·36% of a No. 1 grade firebrick. *Fusion point.* The material as mined fuses between cones 35 and 36, but samples selected specially for their purity gave higher results. *Workability.* The natural andalusite can readily be worked into difficult shapes, this valuable property being due in all probability to the pyrophyllite present. Special refractories can easily be cast with the addition of small amounts of clay. No bond is necessary for the ordinary hand-tamping method, the grains being allowed to bond themselves. *Service test.* After being in use for four months in a tunnel kiln fired with oil to cone 18¼, andalusite blocks forming the tops of the kiln trucks were in good condition and showed no signs of cracking or softening. Previously, fireclay tops broke up rapidly, their average life being 3 to 4 months. Andalusite bricks also gave good results in the side walls of an oil-fired test kiln, which was frequently used for firing ware to cone 32. A mortar made of 100% of finely-ground andalusite gives a thin joint and has proved satisfactory. Summarising, it is stated that the most valuable properties of andalusite are its constancy of volume, its strength under load at moderately high temperatures, its resistance to sudden heating and cooling, and its "workability." Its chief use will be in places where low expansion and high resistance to abrupt changes of temperature are the important requisites.

FORMATION OF MULLITE FROM CYANITE, ANDALUSITE, AND SILLIMANITE.—J. W. Greig (*J. Amer. Cer. Soc.*, **8**, 465, 1925). On being heated, cyanite, andalusite, and sillimanite are decomposed into mullite and silica, or into mullite and a siliceous liquid, the silica being probably cristobalite. There is no definite temperature at which the minerals decompose sharply, or below which they remain unaffected for indefinitely long periods. Cyanite changes at the lowest temperature, and sillimanite at the highest. In the case of cyanite and andalusite, the alteration commences on the surfaces of the grains and advances inward ; whereas, with sillimanite, the change appears to take place throughout the grain. The rate of decomposition increases rapidly with rise in temperature in all three minerals. The mullite crystals newly formed from andalusite and sillimanite are oriented parallel to the original crystals, whilst with cyanite this orientation is determined by the surfaces from which the mullite grows. When cyanite and andalusite decompose, an absorption of heat is observed. The new phases formed by heating the three minerals are of lower density than the original in each case ; that is to say, expansion accompanies decomposition. The expansion due to the alteration of cyanite into mullite and silica is so great, that ware made largely from this mineral would be shattered on firing. It should, therefore, first be converted into mullite and silica at a temperature above 1,400° before being formed into ware. After such conversion, the material becomes more friable, so that it can be ground more easily. With andalusite and sillimanite, however, no trouble due to expansion is to be expected.

THE THERMAL CHANGES OF MAGNESITE. Yoshiaki Tadokoro. (*Research Lab., Yawata Iron Works*, Report No. **4** (2), 1924). The thermal changes in two typical crystalline magnesites obtained from Daisekkio, Manchuria, and widely used in Japan, are reported. The chemical composition of specimens varied widely, two examples being as follows :—

	SiO_2	Al_2O_3	Fe_2O_3	$CaCO_3$	$MgCO_3$	Impurities.
White magnesite	16·62	0·32	0·72	0·90	81·42	Talc and org. matter.
Blue magnesite	20·02	0·14	0·14	0·60	79·03	Serpentine, talc, and considerable amt. of org. matter.

Some specimens contained only 1% of silica. The strength of the magnesites diminished with progressive dissociation and showed a slight increase at 1,300°. Slight losses in weight occur at about 120° in the white magnesite, and about 200° in the blue, probably owing to the expulsion of water. Dissociation of $MgCO_3$ begins at about 400°, and is almost complete at 850° in both specimens; the rate attains its maximum at about 600°. Similar experiments on talc are described. Talc loses about 0·5% of its weight at 80-350° and about 5·5% at 800°-1,150° ; the maximum rate of dissoc. is exhibited at 1,000°C. Whiye specimens expand gradually up to 650°. They then begin to contract, probably owing to the thermal dissociation. They show a slight but sudden contraction at 950°, when $CaCO_3$ in the specimens dissociates. They show a linear contraction of about 3·3% at 1,300°-1,450° where crystallisation of amorphous MgO occurs. Slight changes at 1,450° may be due to the crystallisation of amorphous CaO. Blue specimens show a slight but sudden expansion at 350°-450°, probably caused by the combustion of organic matter. Abrupt changes occur at 650° and 950°, as with white magnesite. Sudden contractions take place at 1,250° and 1,450°. Cooling curves of both magnesites give no indication of transition points. Two white specimens showed linear contractions of about 4·5% and 7·0% at 1,600°, which increased after cooling to about 6·5% and 10·0% respectively, while those of two blue specimens were about 0·5% and -0·2%, increasing to about 2·5% and 1·7% respectively after cooling. For the thermal analysis at 0°-1,300° by the differential method, blue magnesite and alundum powder were used as sample and neutral substances respectively. An endothermal change began at 513°, the lag in temperature attaining its maximum at 652°. The temperature lag began to decrease at 687°, its rate becoming maximum at 757°, and returning to normal at 800°. No change was observable at temperatures where $CaCO_3$ in the sample must have dissociated. Similar experiments on Iyo dolomite are described. Here the endothermal reactions occurred at 710° and 870°, the maximum lag being shown at 810° and 950° respectively. Inverse time curves, *i.e.*, curves showing the relation between temperature and time, required for a rise in temperature of 10°, are given for white and blue samples. In white magnesite, a slight endothermic change occurred at 300°-430°, probably owing to the decomposition of organic matter. Considerable absorption of heat, due to dissociation of $MgCO_3$, began at 520°, attaining its maximum at 630° ; a weak absorption was shown at 900°-950°, possibly due to the dissociation of $CaCO_3$. In blue magnesite, decomposition of organic matter, $MgCO_3$ and $CaCO_3$ is indicated at 300°-430°, 600°-810° and 850°-970° respectively. For the thermal analysis at 1,000°-1,600°C. by the inverse time curve method, a molybdenum wire electric furnace and a molybdenum-tungsten thermo-couple were used. The inverse time curve for blue magnesite shows two distinct heat absorptions at 1,280°-1,320° and 1,420°-1,480° which are probably due to crystallisation of amorphous MgO and CaO respectively. Adsorption of water by the white and blue magnesites, heated at various temperatures, rapidly increases at a firing temperature of 500°, reaches its maximum at 700° and becomes zero at 1,300°. The apparent sp. gr. and hardness of fired blue magnesite are as follows :

Firing temp.	0°	500°	600°	800°	1000°	1100°	1700°
Sp. gr. ..	3·0	2·9	2·7	1·5	1·5	1·6	2·8
Mohr's scale	3·5	5·5	3·5	3·0	2·5	4·5	5·5

36 micro-photographs with detailed descriptions are given. The refractive index of white magnesite increases regularly with the heating temperature up to about 1,280°, then an abrupt rise occurs. S. KONDO.

STANDARD NATURAL SAND.—Sozo Kano (*Jap. Assoc. Portland Cement Eng., Report*, **15**, 71, 1923). The sand produced at Shobuzawa Somagun, Fukushima Prefecture, appears to be more suitable than the standard ground quartz now used in the country. The physical and chemical properties of the sand are compared with those of the standard sands used in domestic and foreign countries:

Countries	Kind	Place of production	Voids (%)	Fineness (Meshes per sq. cm.)				Chem. compn.					
				>64	64–144	144–225	<225	Ig. loss	Silica	Alumina	Fer. ox.	Lime	Total
Japan ..	Stand quartz	Sukegawa, Hitachi	49·32	0·05	58·28	41·38	0·32	0·08	98·02	1·46	0·30	0·16	100·02
	Proposed sand	Shobuzawa, Somagun, Fukushima Pref.	41·79	0·15	55·26	44·41	0·18	0·14	98·74	0·88	Trace	0·20	99·96
Great Britain	Arrived in 1921	Leighton Buzzard, Bedford	40·70	0·90	77·10	14·05	7·91	0·18	97·36	1·32		0·88	99·37
Germany	Arrived in 1920	Freienwalde a/O	41·40	21·46	78·41	0·05	0·00	0·18	98·20	1·00		0·52	99·90
U.S.A...	Arrived in 1915	Ottawa, Ill.	39·60	0·10	97·82	1·94	0·12	0·21	97·66	1·00		0·62	99·49
France..	Arrived in 1920	Leucate, Aude	41·40	58·98	35·29	5·27	0·40	1·42	84.96	7·42	1·22	1·82	96·84

The influence of the standard sands on the strength of 1:3 mortar was studied with a Portland cement, the method of testing followed being that specified by the Japanese Government,

	Tensile str. 1 week.					Tensile str. 1 week.				Crushing str. 4 weeks.					
Standard	Japan	Germany	France	Great Brit.	U.S.A.	Japan	Germany	France	Great Brit.	U.S.A.	Japan	Germany	France	Great Brit.	U.S.A.
Water (%) ..	7·3	6·8	6·8	6·8	6·8	7·3	6·8	6·8	6·8	6·8	7·3	6·8	6·8	6·8	6·8
Strength (kg/sq. cm.)	24·4	21·1	27·6	21·4	27·3	31·6	29·8	31·5	27·0	35·6	260	454	462	396	406

Compared with the standard ground quartz, the proposed natural standard sand increases the tensile strength after 1 or 4 weeks by about 10%, the crushing strength after 1 week by 70-80% and the crushing strength after 4 weeks by 70% (in a 1 : 3 mortar). S. KONDO.

AN X-RAY STUDY OF NATURAL AND ARTIFICIAL SILLIMANITE.—J. T. Norton (*J. Amer. Cer. Soc.*, **8**, 401, 1925). Mixtures of pure alumina and silica in the molecular proportions of 3 : 2 and 1 : 1, and also samples of kaolin and other pure clays, were heated to temperatures of 1,500° to 1,850° and examined by the X-Ray diffraction method. The diffraction patterns given by these materials were all identical and were in exact agreement, in regard both to position and relative intensity of the lines, with the pattern obtained with natural sillimanite, the only exception being the fused 3 : 2 mixture, which produced the corundum pattern. To explain the difference in chemical analysis previously observed (*c.f.* Bowen and Greig, *J. Amer. Cer. Soc.*, **7**, 238, 1924), it was assumed either that additional silica or alumina molecules, arranged at random, occupy the open spaces in the molecule of the compound (in which case, however, considerable scattering of the X-ray beam would have been observed), or, that the two compounds are identical, and that the X-ray method affords a more fundamental analysis of the substance than the chemical method, since the results are not affected by the amorphous glass in which the crystals occur.

II.—MANUFACTURING PROCESSES

MANUFACTURE OF REFRACTORIES BY THE SEMI-DRY-PRESS METHOD.—E. Hagar (*J. Amer. Cer. Soc.*, **8**, 122, 1925). The plasticity of the raw materials should be developed by weathering the moist clay for at least 48 hours, preferably for a longer period. The quantity of water added should be such that, on squeezing the material in the hand, it will ball up into a compact shape and break without being shattered. The percentage of finely ground clay should be sufficient to fill the voids between the coarse particles. It is essential that some form of mechanical mixer should be used above the press so that the fine and coarse particles do not separate out. The press should be fed by a perpendicular chute ; a chute placed at an angle will cause the coarse particles to run ahead of the finer. For the manufacture of large shapes the material must be uniform and homogeneous. With proper care, there should be no difficulty in pressing shapes as large as 24 × 12 × 4 inches. The press must be properly equipped for making various shapes.

PATENTS.

ROOFING TILES.—Ichitaro Kawase (*Jap. Pat.*, 1,939 (1924), 22/10/24). Tiles made of a mixture of clay, bittern and water are fired in a suitable kiln, cooled, again heated to 200°, and painted several times with a mixture of shellac (in alcohol), and powdered copper at 200°. The tiles are strong and water-proof. S. KONDO.

POROUS BRICKS.—K. Horie (*Jap. Pat.*, 2,607 (1924), 12/12/24). A mixture of clay, sawdust, and kokaseki (a kind of pumice) is worked to the required consistency with the addition of an aqueous solution of soft (resin) soap containing sodium silicate. Bricks made from this body are fired in the usual way. S. KONDO.

HEAT INSULATING BLOCKS.—Tokio Hoonzai Co. (*Jap. Pat.*, 61, 468, 22/10/24). A mixture of 300 parts of sawdust soaked in a 2-5% solution of sodium bicarbonate, 600 parts of diatomaceous earth, 50 parts of clay, and 50 parts of plaster of Paris is worked up with a 2-5% solution of sodium silicate and syrup in equal proportions. Blocks made therefrom are fired at 800°-1,000°. S. KONDO.

MAKING BRICKS.—T. Magata (*Jap. Pat.*, 3,899, 25/3/25). A mixture of refractory clay, ferriginous clay, iron powder, and water is pressed, dried, and

fired at a high temperature. Bricks made from the mixture are claimed to be strong and non-absorbent. S. KONDO.

FIRE-PROOF SLABS FOR SAFES, ETC.—R. Aone (*Jap. Pat.*, 61,443, 22/10/24). Slabs are made from a mixture of 50-60 pts. of kokaseki (pumice), 10-20 pts. of asbestos, and 10-20 pts. of slag cement, with water, brine, or a solution of other salt. S. KONDO.

REFRACTORIES.—R. Aone (*Jap. Pat.*, 3,576, Suppl. to *Jap. Pat.*, 719, 6/3/25). A mixture of powdered kokaseki (pumice), calcined magnesite, and asbestos, with or without slag cement, is worked up with a solution of magnesium chloride or magnesium chloride and aluminium acitate.

NEW METHOD OF MAKING POTTERY.—T. Uchida (*Jap. Pat.*, 60,647, 15/5/24). The body contains ground magnesite, clay, a pigmant, and water; *e.g.*, 50 pts. of magnesite, 45 pts. of Kibushi clay, and 5 pts. of rouge. The ware is dried, fired at 800° for 3-5 hours, and then immersed in a solution of magnesium chloride (sp. gr. 1·210) for several hours. S. KONDO.

RUST-PROOFING PINS FOR PORCELAIN TEETH.—K. Shofu (*Jap. Pat.*, 2,600 (1924), 12/12/24). The exposed portion of a nickel or alloy pin fixed in a porcelain tooth, whether gilded or not, is coated with a fusible mixture, which melts during the firing. S. KONDO.

COMPOUNDING AND PREPARATION OF BODIES, ETC.

TALC AS THE PRINCIPAL BODY INGREDIENT IN VITRIFIED CERAMIC BODIES.—R. M. Kraner and S. J. McDowell (*J. Amer. Cer. Soc.*, **8**, 626, 1925). A study is made of the firing behaviour of pure talc and of mixtures containing more than 50% of talc and bonded with clay. Use is made of the phase rule diagrams. The difficulty experienced in firing clay-bonded talc mixtures, owing to the narrow vitrification range, can be met to some extent by the use of mixtures lying close to the forsterite ($2\,MgO{\cdot}SiO_2$) field. The addition of magnesia to the talc, and the use of the minimum quantity of clay, for producing the necessary moulding property, tend to effect this change toward the porsterite composition.

PATENTS.

SEMI-REFRACTORY HEAT-INSULATING COMPOSITION, AND THE METHOD OF MAKING IT.—H. T. Cess, Assr. to The Celite Co. (*U.S. Pat.*, 1,544,433, 30/6/25. A body consisting of diatomaceous earth, a cataytic inversion agent, and water is calcined to produce silica in the form of tridymite, which serves as the principal ingredient of the composition.

POTTERY MADE WITH TALC.—K. Hirano and S. Komori (*Jap. Pat.*, 62,292, 6/2/25). A pottery body is compounded as follows: 25 parts of talc, 30 parts of talc calcined at about 1,250°, 30 parts kaolin or clay, 10 parts felspar, 3-5 parts of magnesite calcined at 800°, and 2-5 parts magnesium chloride; 5 to 10 parts of Sorell cement may be substituted for the last two ingredients. Ware made from this body is glazed after drying, and glost fired. S. KONDO.

MAKING BRICKS.—H. Grönroos (*Engl. Pat.*, 238,229, 6/8/24). A portion of the clay is sintered at a comparatively low temperature and mixed with raw clay to form the moulded bricks, air-drying prior to firing being unnecessary. Fluxes (sodium and potassium compounds and iron oxide) may be added to lower the sintering temperature.

POTTERY BODY.—H. Krum (*Germ. Pat.*, 413,902, 27/5/24). The following ingredients: 1-5 parts of quartz, $\frac{1}{2}$-4 parts grog, 1-5 parts barite, $1\frac{1}{2}$-4 parts talc, 1-5 parts clay, $\frac{1}{4}$-2 parts magnesia, $\frac{1}{4}$-$\frac{3}{4}$ parts sodium chloride, and 3-8 parts water glass, finely ground, are added in the above order and

thoroughly mixed together. A pressure of 200 atm. is applied in forming the ware, which is dried with the exclusion of sun-light and fired to a suitable temperature in a pottery oven. The ware can be quenched at red heat in cold water without cracking.

POROUS INSULATION BRICKS.—H. V. Allen (*Engl. Pat.*, 234,538, 26/2/25). A mixture of 80-87·5% by volume of coke breeze or dust and 20-12·5% of refractory clay is rendered plastic with water, moulded, and fired. The coke is burned out, leaving a porous brick.

REFRACTORY SUBSTANCE.—B. Bell (*Engl. Pat.*, 236,063, 13/8/24). Dried, refined, and finely disintegrated clay containing 50% or more of silica (*e.g.*, from Creech, Dorset, china clay, ball clay, or fireclay being excluded) is made up into a slip, surplus water being removed. Articles are die-pressed from this slip under heavy pressure. The product is fired slowly (1° per min.) to 400°, maintained at this temp. for 1 hr., then fired at the same rate to 750°. The final firing is : From normal to 1,000° in 2 hrs., then to 1,300° in 3 hrs., and maintained thereat for 4 hours. The raw material is dried for 1 week at 35-40°, and then passed through a fine sieve. The slip is made with water at 38° passed through a fine lawn, and allowed to settle for one week.

SHAPING, MOULDING, DRYING, ETC.

MOULDING SILICA BRICKS BY MACHINE.—(*Brick*, **66**, 899, 1925). A large bucket elevator and conveyor travel under the bin where the buckets are filled, moves upward to a height of about 15 ft. and travels backward horizontally to a point where the buckets are emptied into a small hopper. Immediately after the buckets have been emptied, the small receiving hopper is opened by a cam operated by the elevator machinery and the load of silica mud is discharged in a lump into a mould 12 ft. below. Each discharge of mud is sufficient to fill a six brick mould. The excess mud is cut off by a device which consists of a revolving drum about 10 in. in diameter having one edge extending 1½ in. from the face to form a knife. This device is drawn backward and forward over the mould by compressed air. The moulds are set on a steel table, which moves backward and forward under the discharging hopper at right angles to the cutting-off machine. Two men work on each side, placing the moulds and removing the moulded bricks. The operator moves the table under the dumping device by means of compressed air. One end of the table is then under the machine, and on the other end the moulds are being emptied and replaced. When the mould under the dumper has been filled and slicked, the operator causes it to slide out and the mould, which in the meantime has been placed on the opposite end of the table, is brought into position for filling.

DRY-PRESSING FIREBRICKS.—(*Brick*, **66**, 904, 1925). J. S. Unger found, as the result of exhaustive tests, that clays containing from 6·5 to 7% of moisture made the best dry-press bricks. The method developed by Unger has now been applied on a large scale with great success. Neither very fine, nor very coarse raw materials produce good bricks, and careful adjustment of the pressure applied is essential ; hence, a uniform raw material is necessary. The difficulty of feeding clay into the moulds for the different sized pieces and shapes was solved by the use of wooden bins, of different size and shape, which were fixed to the sides of the charging box in order to allow sufficient clay to fill the mould at the large end of the key bricks and also enough to fill the small end properly. All standard sizes and shapes up to $4 \times 9 \times 13\frac{1}{2}$ in. are made without difficulty. The method of operation is as follows : The clay is first allowed to weather for a short time, is crushed, and then stored in large wooden bins. The ground clay is elevated to a wire sieve, and the sieved clay is passed through a chute directly to a steel bin which is cone-shaped to the top. The sloping sides of this bin prevent the materials in it from segregating. The necessity of maintaining uniformity in the physical characteristics of the clay led to the constructing

of a special feeding device for the wet pan. This consists of a cylindrical charging box 18 in. in diameter and 40 in. high, which is fixed to the bottom of the conical bin. It is fitted with gate valves at top and bottom, and it holds exactly the amount of material for one charge to the wet pan. The correct quantity of water required to give a moisture content of precisely 7% is supplied from a small steel tank, placed over the pan and controlled by a float valve. The wet clay is broken up by being passed through a machine consisting of a roller 12 in. in diameter and 24 in. long, in which steel pins, projecting about 2 inches, are inserted at frequent intervals. The roller revolves at high speed and the pins pass through the spaces between similar pins fitted in a stationary plate. From this machine the clay falls directly into the charging box of the press.

KILNS, OVENS, MUFFLES; FIRING TECHNIQUE, ETC.

NOTE ON COMPARISON OF ENGLISH WITH ORTON PYROMETRIC CONES.—S. S. Cole (*J. Amer. Cer. Soc.*, **8**, 462, 1925). English cones 10 to 32 were tested in a pot furnace to obtain the corresponding values in Orton cones. Great irregularity in the fusion temperatures of the English cones was observed. English cones 26 to 32 subsided at temperatures varying from 50° to 90° lower than the squatting temperature assigned to them.

REFRACTORY MATERIALS IN CARBONISING PRACTICE.—A. H. Middleton (*Gas J.*, **172**, 163, 1925); *Gas World, Coking Sect.*, **13**, 7/11/25. The relative efficiencies of fireclay, semi-silica, and silica refractories for the construction of retort settings are discussed at length. The advantages of silica are emphasized. A special cement is necessary which will have a refractoriness comparable with that of silica and which will give an adhesive joint, without cracks.

THE USE OF RADIATION PYROMETERS ON REFRACTORY KILNS.—C. B. Thwing (*J. Amer. Cer. Soc.*, **8**, 115, 1925). In order to cover the whole range of the temperature scale from water-smoking to the finish, with a chart having an open scale, a two galvanometer recorder is used, one of which records temperatures up to 1,600° from a base thermocouple, whilst the high temperatures are recorded from a radiation receiving tube. Each galvanometer records two kilns, distinguished by dash and dot, and each recorder deals with two low and two high kilns simultaneously. The mounting consists of a small refractory hollow block, or muffle, about 7 inches square (inside), the closed end of which projects a few inches into the crown of the kiln. The top of the muffle is closed by a flanged cover having a circular hole, through which the couple is inserted. When a temperature of 1,600° is reached the thermocouple is disconnected and the radiation tube is fixed in position above the hole and connected to the same wires. At the same time the necessary change in the recorder connections are made at the plug switchboard in the pyrometer room. Under certain conditions, the small muffle may be omitted and the tube pointed directly at the ware. In this case, means must be provided to protect the instruments from occasional outrush of flames through the opening.

Patents.

ROTARY KILN.—C. J. Tomlinson (*U.S. Pat.*, 1,544,504, 30/6/25. The refractory lining of a rotary kiln is formed of projections arranged so as to pass through the charge without propelling it. Each projection has a number of heat-absorbing faces, and a cutting edge, near to which is a rough, ploughing surface.

LIQUID WASH FOR REPAIRING FURNACE LININGS.—E. Holley, Assee. of D. H. Meloche (*Engl. Pat.*, 235,505, 11/3/25). The mixture consists of 70 parts by wt. of water, 5 parts of sodium silicate (Grade C., $5Na_2O.11SiO_2.46H_2O$), and 25 parts of powdered fireclay. The wash is sprayed on the heated surface in successive layers.

TUNNEL KILN.—N. Lengersdorff (*Engl. Pat.*, 236,229, 26/2/24). The heat from the cooling zone is utilised to heat air for the preheating zone to which it is passed at a point between two separate outlets for the gases. In the preheating zone, two groups of outlets are arranged one on each side of valve-controlled hot air inlets. The flue connecting each group to the stack can be regulated independently. The hot air inlets communicate with a passage in the roof of the kiln, to which air is delivered from recuperators in the side walls of the cooling zone.

FIRING ARCHITECTURAL TILES.—H. Matsumura (*Jap. Pat.*, 61,482, 22/10/24). A number of triangular pins are inserted into holes, arranged stepwise in two opposite sides of a deep, rectangular saggar. A glaxed tile with 4 projections is set, face downwards, supported on 4 pins. On this tile a second glaxed tile, without projections, is placed, face upward. The projections are removed after firing. S. Kondo.

FURNACE CHARGER.—Soc. Anon. des Usines Lambot (*Engl. Pat.*, 234,738, 29/6/24). A charging device for gas producers etc., consists of a feed-screw with a hopper and a rotary distributing cone driven at a different speed than the screw.

RETORT SETTINGS.—H. J. Toogood and Dempster and Sons (*Engl. Pat.*, 234,947, 3/4/24). To allow for initial and after-expansion of the silica brickwork, the edge bricks of the walls are staggered, so that all do not come into contact with the pier walls, expansion gaps being left between bricks in the same course.

TUNNEL KILNS.—H. T. Padelt (*Engl. Pat.*, 235,459, 13/11/24). The heating flues or chambers, running along side the walls of the kiln, are provided with vertical pipes, open at each end, which pass through the centre of the flue from top to bottom, thus permitting circulation of the kiln atmosphere. The kiln may have two or more superposed flues of this type.

ROOFING-TILE KILN.—M. Sugiyama (*Jap. Pat.*, 2,606 (1924), 12/12/24). In a rectangular kiln with fire-boxes at both ends, a latticed wall is built between the kiln chamber and each fire-box. The kiln has two straight bag-walls with holes inside the latticed walls. Most of the flame enters the kiln chamber upwards through flues built under the kiln floor. The products of combustion escape from the chamber through an opening in the upper part of each side wall. S. Kondo.

ROOFING-TILE KILN.—S. Fujiwara (*Jap. Pat.*, 2,250 (1924), 19/11/24). In a rectangular kiln with fire-boxes at the front, the flame enters the kiln chamber through three sets of holes in its front wall: (1) Several big holes beneath the kiln floor which make the flame enter the kiln chamber upwards; (2) Many small oblique holes built half way up the wall; (3) Several holes of medium size in the upper part of the wall. The products of combustion escape from the kiln chamber through holes in the upper part of the rear wall and pass downwards through a narrow chamber behind the wall. S. Kondo.

TUNNEL KILN.—The Toyo Toki Co. (*Jap. Pat.*, 3,570, 4/5/25). A tunnel kiln, which has two combustion chambers with corrugated walls in its sides, and which fires the wares by means of hot circulating air, is connected with a drying arrangement, in order to lead the dried air into the kiln at a point close to its mouth end. S. Kondo.

GLAZES, ENAMELS.

ENAMELLING DEFECTS DUE TO CAST IRON.—A I. Krynitsky (*J. Amer. Cer. Soc.*, **8**, 618, 1925). Insufficient data are available to support the conclusions drawn by Malinovszky (Trans., **24**, 12A, 1925), regarding enamel defects due to carbon. The results of tests are cited which would indicate that the quantity of graphite and the size of the graphite flakes are more important than the amount of combined carbon present in the iron.

In a study of the causes of blistering of enamels other factors, such as the casting temperatures and rate of cooling, the preliminary heat treatment and the temperatures employed, the time of exposure to high temperatures, and the extent of decarburisation of the surface of the iron, must also receive consideration. The presence of large rather than very small graphite particles may be desirable if the iron is treated only by sand blasting and no preliminary annealing is applied.

NOTES ON THE COLOUR OF ANTIMONY ENAMELS,—W. E. Manson, (*J. Amer. Cer. Soc.*, **8**, 437, 1925). Antimony oxide of American origin, of only 92% purity, and grey in colour, gave enamels of an opaque, cream colour, whilst a purer material containing 98% of antimony oxide and pure white in colour, produced enamels of poor opacity and unsatisfactory in colour. Experiments indicated that the insoluble impurities in the American material exercised a decided effect upon the colour of the enamel, but the precise nature of this effect was not determined.

Patents.

ENAMEL COMPOSITION.—H. S. Cooper (*U.S. Pat.*, 1,517,618, 2 Dec.,1924). An enamel composition contains zirconium oxide and an opacifying compound of a metal having an atomic weight of about 119, in the approximate proportion of 3 to 2 parts by weight.

COLD GLAZES.—C. J. Tidy (*Engl. Pat.*, 234,707, 12/11/24). The mixture contains Portland cement, alumina, and fused calcium chloride solution. Stains or pigments may be added. The glaze may be applied by spraying, or by other methods.

ENAMELLING APPARATUS (KILN).—C. Dressler, Assr. to American Dressler Tunnel Kilns, Inc. (*U.S. Pat.*, 1,552,475, 8/9/25). Both sides of a flat article are enamelled in a muffle kiln by setting up convection current circulation of the kiln atmosphere in a direction transverse to the length of the kiln. The articles are supported in a horizontal position, with the upper surface exposed to radiant heat from the roof of the kiln and the lower sides to radiant heat from the hot kiln walls.

COLOURS, DECORATIVE PROCESSES, ETC.

Patents.

UNDER-GLAZE DECORATION WITH PASTED PATTERN PAPER.—J. Wakabayashi (*Jap. Pat.*, 3,898, 25/3/25).—Thin papers with rice starch or gum arabic patterns are applied to soft biscuit ware, moistened with water, and painted with pigments. The latter penetrate the paper and decorate the ware. S. Kondo.

PRODUCING LUSTRES ON GLAZED POTTERY.—S. Kanashina (*Jap. Pat.*, 62,280, 5/2/25). Buttons, beads, or other glazed wares, are drawn from the kiln at 500°-600°, or reheated to this temperature after firing, and placed in a powdered volatile metallic compound, *e.g.*, arsenious acid, the chloride or nitrate of bismuth, tin, iron, copper, strontium, uranium, cobalt, chromium, gold, silver, or platinum. S. Kondo.

PREPARATION OF LIQUID GOLD.—J. Ishikawa and R. Hattori (*Jap. Pat.*, 4,191, Suppl. to No. 35,932, 10/7/25). Sulphur-balsam is added to a solution of gold chloride and the mixture is heated over a water-bath. The gold sulphoresinate thus prepared is washed and dried, resinates of rhodium and bismuth, or those of rhodium, bismuth, aluminium, and chromium being then added. The product is dissolved in a mixture of refined oils. S. Kondo.

PREPARATION OF LIQUID GOLD.—T. Yoshioka (*Jap. Pat.*, 4,425, 22/4/25). A balsam of gold sulphide, obtained by treating a solution of gold chloride with sulphur-balsam, is washed, dried, and made up into a viscous

solution with a solvent. Liquid gold is prepared by adding cobalt resinate S. KONDO.

STENCILS FOR DECORATING POTTERY.—J. T. Fell (*Engl. Pat.*, 232,646, 20/11/23). Stencils are attached to a wire frame, which is provided with a handle, and hooks for supporting the device on the article. The stencils stand out from the main part of the frame.

LIQUID GOLD CONTAINING A NICKEL SALT.—I. Shoji (*Jap. Pat.*, 1,937 (1924), 22/10/24). Nickel resinate is added as a constituent of liquid gold. S. KONDO.

DECORATING POTTERY WITH GOLD.—Nippon Toki Co. (*Jap. Pat.*, 61,199, 15/9/24). A transfer containing no gold is applied to the varnished surface of pottery and fired on at 800-850°. The ware is then painted with a 3-5% gelatine solution, a gold transfer of special design is applied and fired on at 600-850°. S. KONDO.

PLANT AND MACHINERY, ETC.

A PATENT AUTOMATIC MACHINE FOR THE MANUFACTURE OF ORNAMENTED CLAY AND CEMENT TILES BY THE SEMI-DRY-PRESS METHOD.—J. Roux (*Cer.*, **28**, 25, 1925). The machine consists essentially of a circular transporter, having an intermittent rotating movement and carrying six moulds under the different manufacturing devices, of which there are eight:—(1) An ordinary hydraulic press for two or four tiles; (2) A hydraulic lifter driven automatically by a piston distributor; (3) An automatic hydraulic mould cleaner driven by a distributer; (4) A device for admitting and ejecting the patterns; (5) An automatic agitator, which causes the powder to penetrate into the finest parts of the design; (6) a rotating, double-acting pattern cleaner, connected by control valves to the air pump; (7) A rotating colour compositor, which discharges an equal quantity of powder into all parts of the design above the cover plates; and (8) A ground mass filler, which automatically sifts a given quantity of coarse grained powder over the colour layer. These eight distinct devices are supplemented by the hydraulic distribution arrangement, which has been studied carefully, so that it can be operated by hand in case of need; by the air pump, with filter and dust collector; by the air compressor, and an 8 h.p. electric motor, which drives at one end of the shaft the air pump, and at the other the speed controller. The machine is capable of turning out from 380 to 750 tiles per hour in five colour designs, according to the type of press used, and it requires the attention of one man only.

III.—FINISHED PRODUCTS: TESTING, ETC.

WIDE-SHED INSULATORS (PIN TYPE).—W. Cordes (*Keramos*, **3**, 559, 1924). The manner in which the German wide-shed type of insulator developed from the first Delta type is described. Wide sheds were added to a central core in accordance with the distribution of the lines of force. The core was so shaped that the lines of force did not meet the porcelain at a sharp angle. The method of conducting the flash-over test is described. The type of nozzle used for spraying the insulators to simulate rain is important. In Germany, the flash-over tension is measured after spraying for 15 min. The method of measuring the breakdown strength in oil is criticised as giving results which are not of great practical value. Wide shed insulators are so constructed that the breakdown strength in oil is on an average, 50% higher than the flash-over tension. To ensure a uniform distribution of electrical stress, the middle portion of the three-part wide-shed insulator is made somewhat thicker than the head and socket. Greater mechanical strength was attained by shortening the length of the pin, which does not extend to the circular groove around the top. For a working tension of 70 k.v. the length of the pin in the wide shed insulator is 255 mm., compared with 430 mm. for the corresponding Delta type. The two types do not differ greatly in weight. When cementing the parts together, the layer of cement must be as thin as possible. The cemented surfaces of the wide-shed in-

sulator are much smaller than in the case of the Delta type. Some German makers recommend that the parts should be glazed together, whilst in one instance the experiment has been tried of firing the parts together, so that the finished insulator practically possesses the properties of a one-piece insulator, *Texture.*—The porcelain must be as tough as possible, to withstand shock, changes of temperature, and strain caused by the cement. High mechanical and high electrical strength are difficult to combine. It is suggested that the fuchsin test for porosity should be more severe; the porcelain should be immersed in the solution under a pressure of 15 atm. for about half an hour. A suitable body has a high clay-substance content and is fired to a very high temperature. The *glaze* should have a high melting point and a maturing temperature adjacent to that of the porcelain. It must have a thoroughly dense surface and should feel soft and greasy to the touch. The temperature of the hot water in the quenching test varies as follows:—For cemented pin insulators, 90°; glazed pin insulators, 65°; suspension insulators, 75°; the cold water has a temperature of 15° in every case. Near chemical works, or the sea coast, the insulators must be cleaned periodically to remove deposits of salts which accumulate beneath the sheds. They should, therefore, be so made that the sheds lie a suitable distance apart.

THE RELATION OF STRUCTURE AND COMPOSITION TO THERMAL EFFICIENCY OF REFRACTORIES WHEN USED IN REGENERATORS.—S. M. Phelps (*J. Amer. Cer. Soc.*, **8**, 648, 1925). The relative rates of heat transmission in fireclay, silica, diaspore, fused alumina, and silicon carbide refractories were determined by heating 9-inch bricks as uniformly as possible to 1,260° and cooling at a uniform rate, the temperatures at the surface and at the centre being recorded at short intervals. The quantity of heat released during cooling, expressed in B.Th.Us., varied considerably for the different bricks. The efficiency of a checker brick depends upon the thermal capacity and the thermal diffusivity of the material, and varies directly with the apparent sp. gr. The denser the brick, therefore, the more suitable for use in regenerators. Hence, dense clay bricks proved more efficient than silica bricks. Silicon carbide has a high thermal conductivity, but a low thermal capacity. The effect upon the thermal efficiency of completely glazing the surfaces of a brick was negligible.

THE LABORATORY TESTING OF PLASTIC REFRACTORIES.—R. F. Geller and W. L. Pendergast (*J. Amer. Cer. Soc.*, **8**, 441, 1925). An investigation of the physical and chemical properties of plastic refractories was undertaken, with a view to the development of specifications for this product. Twelve brands were submitted to the usual physical tests (quenching, softening point determination, refractoriness, water content, shrinkage, chemical composition, etc.). The results of the investigation are as follows: The water content varied from 9·3 to 15·7%, the average being 12%; the average drying shrinkage was 1·5%; the average modulus of rupture (dry) was 48·6 lb. per sq. in.; screen analyses indicated that the materials contained, on an average, 60% grog, varying considerably in size, and 40% plastic clay; chemical analysis—43·8-65·6% SiO_2, 30·9-50·8% Al_2O_3, 0·6-1·9% Fe_2O_3, 0·2-2·3% TiO_2, and, by difference, 0·2-2·4% alkalis; the softening points ranged from 30 to cone 34; the resistance to spalling was uniformly high, the materials resisting from 15 to 20 quenchings; in the endurance test specimens measuring $10 \times 4{\cdot}7 \times 2{\cdot}7$ m showed an average deflection of $\frac{3}{16}$in. when refired for 72 hours at 1,450°C. while placed over a 7-inch span and supporting a weight of 6 lb. at the centre.

A STUDY OF THE FACTORS INVOLVED IN THE SPALLING OF FIRECLAY REFRACTORIES WITH SOME NOTES ON THE LOAD AND REHEATING TESTS AND THE EFFECT OF GRIND ON SHRINKAGE.—M. C. Booze and S. M. Phelps (*J. Amer. Cer. Soc.*, **8**, 360, 1925). The tendency of fireclay refractories to spall is largely dependent upon the following three factors: coefficient of expansion, diffusivity or rate of tem-

perature change, and elasticity. A number of fireclay mixtures, varying widely in composition and structure, showed greater differences in their coefficients of expansion than were expected. The expansion between 0° and 650° bore a direct relation to the silica content, and it was also governed to a small extent by the temperature of firing. The lowest value was obtained when the test piece was fired at an extremely high temperature, the result being the formation of a large amount of glass. In computing the expansion for furnace design, values from 0·000004 to 0·000006 should be used for bricks containing from 50 to 60% of silica, instead of the figure 0·0000075, which has hitherto been in use. The degree of grinding had no effect on the thermal expansion. Although the mixtures tested differed greatly in structure and compositions, only small differences were detected in the diffusivity, or the rate of rise in temperature under identical conditions of heating. Finely ground bricks showed slightly higher temperatures at the cooled end than the coarsely ground. The test pieces varied between rather wide extremes in porosity, so that it would appear that the structure is not of great importtance when choosing bricks for checkers in regenerators. The results of special tests for elasticity showed very considerable variations. Plastic and permanent deformation took place at surprisingly low temperatures. The property of plastic flow at low temperatures gives the effect of elasticity, and the particles within the refractory body may move under a spalling stress without crushing taking place. Coarsely ground mixtures assumed plastic deformation much more readily than the more finely ground bodies. A number of the bricks were subjected to the spalling test in order to check the results of the investigations. The rate of temperature change had no effect on the spalling results. The coefficients of expansion and the elasticity values, however, varied greatly. Although the spalling tendency varied almost inversely with the coefficient of expansion, the controlling factor in spalling was elasticity, which can be varied over wide limits. With one exception, the results of the elasticity tests coincided with those of the spalling tests. The results of under-load tests (25 lb. per sq. in. at 1,350°) indicated that the degree of firing had a greater influence than the grinding upon the deformation under load. The influence of the degree of grinding upon the drying and firing shrinkage was, however, especially pronounced. The secondary expansion produced in certain bricks upon reheating was shown to be dependent both upon the rate and the temperature of heating.

SELECTION OF FIREBRICKS BY COMPARATIVE TESTS; METHOD OF MEASURING THE TEMPORARY EXPANSION OR CONTRACTION AT VARIOUS TEMPERATURES.—F. A. Kohlmeyer (*J. Amer. Cer. Soc.*, **8**, 313, 1925). The tests to which the about 30 samples were subjected were: the spalling test, cold-crushing strength, under-load test at high temperatures, permanent linear expansion or contraction, temporary thermal expansion, cone softening temperature, and coal-ash slagging test. The spalling test was conducted as usual, except that the quenching was repeated 10 times only. Under-load tests were run with pressures of both 25 and 40 lb. per sq. in. on the bricks. The temporary thermal expansion was determined by a new method. Two holes about half an inch deep and 7 inches apart were drilled in the front top edge of each brick. Cones having a fusing temperature well above that of the test furnace were cemented upside down into these holes with carborundum cement, in such a way that they projected about ¼ inch above the face of the brick. Two one-inch carborundum tubes were sighted on to the cones and extended from the face of the test pieces completely through the bricked-up door. A surveyor's transit was mounted in front of the furnace in such a position that the cones could be sighted through the transit and the tubes. The telescope of the transit could be inserted through a vertical plane and focused on a steel scale mounted at a suitable distance from the transit, so as to give sufficient magnification of the distance between the cones. Readings were taken at room temperature and at 1,090° and 1,370°. For the slagging test, cones were made up of the

ground brick material and varying amounts of coal ash.

THE PUNCTURE VOLTAGE OF PORCELAIN.—T. Toda (*The Tokio Industrial Lab.*, Report **19,** No. 1, 1924). The puncture voltage of porcelain, composed of 30-70% clay, 10-50% felspar and 50-80% quartz and fired at Seger cone 9, 12 or 15 for 18, 22 or 26 hrs. respectively, was studied. The sources of clay were (*a*) Gairome (highly plastic kaolin), (*b*) Kibushi (ball clay), (*c*) Shirae (kaolin)+Gairome, (*d*) Shirae+Kibushi or (*e*) Korean kaolin (very pure kaolin)+Gairome. In testing, a porcelain disc, 14 cm. diameter and 5 mm. thick, was placed between a needle electrode and a steel disk in oil. The composition which gave the best result in each group are as follows :

Group	Gairome	Kibushi	Shirae	Korean kaolin	Felspar	Quartz	Firing temp.	Puncture voltage
a ..	50	—	—	—	40	10	Cone 12	65,000
b ..	—	60	—	—	10	30	,, 12	67,500
c ..	25	—	35	—	10	30	,, 15	74,500
d ..	—	25	45	—	10	20	,, 15	76,800
e ..	25	—	—	45	30	—	,, 12	78,750

Conclusions : (1) The best results are obtained with bodies rich in lean kaolins and poor in plastic clays ; (2) Shirae bodies are best fired at Cone 15 instead of Cone 12 in the other bodies ; (3) Increase of clay in the body tends to raise the puncture voltage ; (4) The highest voltage in a body is given at its minimum apparent sp. gr. Experiments with bodies containing magnesite, limestone or various frits, $RO.Al_2O_3.6SiO_2$ as flux, failed to show any particular results. S. Kondo.

Patents.

TESTING POTTERY.—W. and A. J. Podmore (*Brit. Pat.*, 227,139, 12 July, 1923). Articles of pottery are tested for defects due to different coefficients of expansion between body and glaze in a machine , in which the article is attached to one end of a pivoted arm and is immersed alternately in a hot and a cold bath. The articles are tested for chipping and breaking in apparatus of the pendulum type.

V.—GLASS GENERAL.

FUNDAMENTALS OF HEAT FLOW IN MOLTEN GLASS AND IN WALLS FOR USE AGAINST GLASS.—G. V. McCauley (*J. Amer. Cer. Soc.*, **8,** 493, 1925). Assuming Wamsler's value of 0·96 for the absorption coefficient of a rough clay block, a formula is evolved which expresses the total heat flow by radiation and convection per hour per sq. ft. from a block surface as a function of its temperature. Curves are constructed from this relation. Similarly, the flow of heat by conduction through the block (which is the same in amount) is expressed by a simple relation. The practical application of these two relations is explained. The thermal conductivity of a flux block was determined experimentally ; the results show fairly close agreement at low temperatures with silica and fireclay bricks, but at higher temperatures the tendency to increase is more pronounced. The flow of heat through molten glass was determined by obtaining temperature gradients simultaneously in the glass and in the blocks, the ratio of these gradients being taken as the ratio of the effective conductivity of molten glass to that of the flux block in contact therewith. A marked difference was observed between the effective conductivity of the molten glass and that of the block material. The former increased rapidly with a rise in temperature, due probably to increased convection. The existence of convection currents in molten glass is demonstrated by photographic reproductions.

THE DENSITY AND INDEX OF REFRACTION OF GLASS IN RELATION TO ITS COMPOSITION.—A. N. Finn and H. G. Thomson (*J. Amer. Cer. Soc.*, **8,** 505, 1925). The published data on the relation between

the density, refractive index, and composition of glasses of the silica-soda-lime series are critically examined. From the equations: $D = d_1 + d_2 + d_3 \ldots$ and $d_x = a(p+c)^b$, in which D is the density of the glass, d_1 d_2 and d_3 are the partial densities due to the constituent oxides, p is the percentage of these oxides, and a, b, and c are constants which differ for each oxide, the density of these glasses may be computed with greater accuracy and over a wider range of composition than by other methods. Similar relations are observed between the index of refraction and composition, but the values of the corresponding constants have not been satisfactorily established. It is predicted that tables will eventually be prepared from which it will be possible to determine the composition of a glass from its density and index of refraction.

PATENTS.

CONTINUOUS FURNACE FOR GLASS MANUFACTURE.—Manufactures des Glaces et Produits Chimiques de St. Gobain, Chauny et Cirey (*Engl. Pat.* 225,837, 17/11/24). A melting chamber and one or more firing chambers are constructed as individual units, in separate blocks of masonry, being heated independently one of the other. Electrically heated channels or passages connect the various chambers.

MAGNESIUM-BOROSILICATE GLASS.—V. Skola (*Engl. Pat.*, 239,349, 20/8/24). Magnesium oxide is introduced into a glass frit in the form of magnesium borates or pyroborates, obtained by calcining a mixture of boric acid and magnesium oxide, or of substances which produce boric oxide and magnesia when calcined.

TREATING GLASS DURING ANNEALING.—J. Bennett (*U.S. Pat.*, 1,553,283, 8/9/25). Glass articles, while hot, are placed in an air-tight receptacle, from which the air and gases are subsequently exhausted.

GLASS BLOWING MACHINE.—W. F. Cargo (*Engl. Pat.*, 234,203, 1/3/24). A machine for making glass bottles, etc., has two sets of reciprocating moulds, the parison moulds being alternately brought to the charging position and returned to the transfer position, and the finishing moulds alternately advanced to the transfer position and withdrawn to the blowing position.

GLASS FILTER.—Tokio Electric Co. (*Jap. Pat.*, 4,429, 22/4/25). The filter consists of small grains of quartz glass fused together so as to form a porous mass. S. KONDO.

GLASS MELTING FURNACES.—T. Teisen (*Engl. Pat.*, 238,562, 14/8/25; Addn. to E.P. 194,819). The recuperators are divided into two parts separated by the glass pit, the two parts being accessible.

GLASS; POTTERY MATERIALS.—F. M. Ekert (*Engl. Pat.*, 238,690, 5/8/24). A flux consisting of aluminium fluoride or silicon-aluminium fluoride is added to silica or aluminium silicate, or both. Magnesium fluoride and silicon-magnesium fluoride are used to produce stone-like ware.

VI.—CEMENT, CONCRETE, MORTARS, ETC.

CEMENT MANUFACTURE.—J. Watson (*Ind. Chemist*, **1**, 231, 1925). A general description of the method of manufacture, control of raw materials, etc., is given.

METHOD OF DETERMINING THE FINAL SET OF PORTLAND CEMENT.—K. Shioda and S. Kajiwara (*Jap. Ass. Portland Cement Eng.*, Report **16**, 1924). According to Japanese Portland cement specifications, the final setting is held to be completed only when the Vicat needle will not penetrate the mass. Recent investigations have indicated grave objections to this method, and it is recommended that the final setting should be considered finished the moment the needle sinks about 0·25 mm. into the mass. S. KONDO.

REVISED METHOD OF DETERMINING THE SETTING TIME IN THE CEMENT SPECIFICATION.—K. Shioda and S. Kajiwara (*Jap. Ass. Portland Cement Eng.*, Report **16,** 1924). The influence of temperature upon the setting time has been studied. It is proposed that the setting time should be determined at a temp. of 15°-25°. S. KONDO.

THE RELATION BETWEEN FINENESS AND STRENGTH OF PORTLAND CEMENT.—S. Inokuchi (*Jap. Ass. Portland Cement Eng.*, Suppl. to Report **14,** 17, 1923). The tensile strength of neat Portland cement briquettes increases with the fineness of grinding until a certain limit is reached, beyond which it begins to decrease. Such a limit is shown with a Japanese clinker when it is ground to leave a 6% residue on a 4,900 mesh per sq. cm. sieve. The tensile and crushing strength of 1 : 3 mortar briquettes increase with the fineness of the cement. S. KONDO.

THE ADDITION OF VOLCANIC ASH TO PORTLAND CEMENT.—Ki Shoji (*J. Jap. Cer. Ass.*, **33,** No. 386, 41, 1925). The action of volcanic ash in Portland cement mortar for marine construction is probably due to the formation of hydrated lime compounds from the soluble silicic acid in the volcanic ash and the calcium hydroxide from the cement, and also to the action of the hydrated lime compounds which fill the pores in the structures and make them waterproof. The effect on the setting time of mixing 0-200% of five different volcanic ashes to slow-setting Portland cements is reported. The results may be classified as follows : (1) Retardation of only final set ; (2) excessive acceleration of initial set as well as retardation of final set, and (3) excessive acceleration of both initial and final sets. Of five volcanic ashes, only *A* belonged to (3) ; *e.g.*, 20% changed the initial and final sets of a cement from 5 hr. 23 min. and 9 hr. 33 min. to 0 hr. 4 min..and 1 hr. 37 m. respectively. Analyses of the five volcanic ashes are as follows :

				Treated with NaOH and HCl solutions.				
	Moist	Ig. loss	Sol. SiO_2	Sol. Al_2O_3	Sol. Fe_2O_3	Sol. CaO	Sol. MgO	Alkalies
A ..	4·45	14·81	33·26	28·03	8·30	0·57	1·03	1·92
B ..	1·62	6·19	38·16	14·56	2·31	1·14	0·63	5·64
C ..	3·63	10·10	45·21	11·75	1·91	1·32	0·77	4·81
D ..	0·80	1·83	22·92	7·20	1·64	2·72	0·44	3·95
E ..	2·43	6·29	30·20	11·27	4·67	2·44	1·15	5·68

The abnormal acceleration of "*A*" is probably due to its high content of soluble alumina. The author treated "A" and "*B*" with a solution of caustic soda, acidified the solutions with HCl and finally obtained precipitates of silica and alumina with ammonia ; the analyses are as follows :

	Ig. loss	Silica	Alumina
Ppt. from *A* ..	27·82	35·04	34·84
,, ,, *B* ..	25·94	45·70	26·62

The action of these precipitates on a cement was as follows : (Temp. of room = 20·5°).

	Portland cement	+40% *A*	+4% ppt. from *A*	+4% ppt. from *B*
Water (%) ..	25·0	32·2	25·5	25·5
Initial set (hr. min.)	3·13	0·03	0·03	0·38
Final set ..	5·23	0·08	0·22	3·13

The influence of SO_3 in the cement on the action of volcanic ash was studied. The average content of SO_3 in nine cements, whose setting times were accelerated by *A* was 1·16%, while that in nine cements which remained slow setting was 1·35%. The former kind of cement can always be changed to the latter by adding gypsum, so as to bring the SO_3 content to approximately 1·6%. S. KONDO.

PATENTS.

MANUFACTURE OF BLAST FURNACE CEMENT.—K. Grün (*Germ. Pat.*, 414,424, 16/6/22). During the grinding of blast furnace slag and Portland cement clinker, which may have a high lime content, the mill is kept hot by artificial means. Hot grinding increases the initial strength of the cement and counteracts the tendency of the clinker to expand.

MANUFACTURE OF PORTLAND CEMENT.—Façoneisen-Walzwerk L. Mannstaedt & Cie. A. G., and E. Best (*Germ. Pat.*, 414,788, 18/8/22). With limestone or marl as the starting material, blast furnace dust, either dry or in slurry form, is added as the argillaceous ingredient, the mixture being burnt in the usual way.

BURNING PLASTER OF PARIS FROM WASTE PLASTER.—E. Fischer (*Germ. Pat.*, 412,811, 12/12/22). The size of the pieces of waste plaster to be burned varies directly with the time and temp. of burning, and with the time necessary for dehydration, and inversely with the density of the individual pieces and with the setting time of the finished product. For a slow-setting product the pieces must be as small as possible, and *vice versa*.

MAKING ARTIFICIAL MARBLE.—H. J. Kimmel and L. A. Harris (*U.S. Pat.*, 1,550,077, 18/8/25, A mortar of pasty consistency is dried in forms at 80° for about 24 hrs., then removed from the forms and subjected to a temperature of 95° for a similar period, after which the temperature is slowly increased to 125° during a period of about 36 hrs.

MAKING ARTICLES (TILES) FOR BUILDING.—W. H. Graveman (*U.S. Pat.*, 1,549,867, 18/8/25, Pulverised coal tar pitch is mixed with pulverised slag, and the mixture is heated to about 100°, pressed to the desired shape, and then subjected to a higher temperature to cause carbonisation.

IMITATION GRANITE.—K. Sano and T. Shimizu (*Jap. Pat.*, 3,218, 16/2/25). Tiles pressed from a mixture of ground granite, felspar, kaolin, soda-ash and water are dried, whereupon the soda-ash appears on the surface as a white powder. Calcined sand is then applied to the surface. The soda-ash serves to vitrify the surface of the tile and to bind the applied sand. S. KONDO.

CEMENTS AND MORTARS.—O. Tetens and Rekord-Zement Industrie Ges. (*Eng. Pat.*, 234,233, 25/3/24). Mixtures containing siliceous, calcareous, and bituminous ingredients, *e.g.*, bituminous limestone and siliceous earth or clay, or bituminous oil shale and limestone or lime and clay, are burned without fuel to a temp. below vitrification point, oil being recovered.

BINDER COMPOSITION FOR ABRASIVES, ETC.—H. R. Power, Assr. to Carborundum Co. (*U.S. Pat.*, 1,553,105, 8/9/25). A cement mixture containing calcium hydrate is subjected to the action of carbon dioxide to convert the calcium hydrate into calcium carbonate.

UTILIZATION OF WASTE CONTAINING CARBON.—Gewerkschaft ver. Constantin der Grosse (*Germ. Pat.*, 410,458, 28/12/22 ; Addn. to *Germ. Pat.*, 373,846). Waste products, *e.g.*, washings, are distilled or evaporated down, the residue pressed into brick form and fired to produce building bricks.

MANUFACTURE OF ARTICLES (BRICKS, ELECTRODES) OF CARBON.—Gelsenkirchener Bergwerks A. G. (*Germ. Pat.*, 413,442, 1/5/21). Suitable natural carbon in the form of a slurry, which has been washed to remove the ash, is used as raw material. The product has a high electrical conductivity.

PREPARING SINTERED HYDRAULIC BINDING MATERIALS AND SINTERED RAW MATERIALS, HYDRAULIC AND NON-HYDRAULIC. —G. E. A. Cuylits (*Engl. Pat.*, 238,340, 2/7/24). A small quantity of one or more catalysts, having a higher sintering temperature than that of the burnt product, is added to the cement mixture before sintering or clinker formation takes place. In composition such catalysts may be identical

with or similar to the final product, provided that they have been burnt to a higher temperature than that of the product to be obtained. They may also contain a small proportion of metal oxides or other metal compounds. The catalytic action develops better if the sintering is carried out in a reducing atmosphere, or intermittently under oxidising and reducing conditions.

IMPROVEMENTS IN CEMENT KILNS.—G. V. Evers (*Engl. Pat.*, 238,407, 9/10/24). The firebrick linings of cement kilns are roughened, scoured, indented, or impregnated with cement clinker, in order to facilitate the formation on the bricks of a protective coating of cement clinker.

VII.—CHEMICAL AND ANALYTICAL PROCESSES.

DETERMINATION OF MAGNESIA IN PORTLAND CEMENT.—K. Mizobuchi (*Jap. Ass. Portland Cement Eng.*, Suppl. to Report **14**, 1923). In the determination of silica and lime the silica residue must not be heated above 110°. Excess of ammonia must be avoided in the precipitation of calcium, the precipitate must be filtered in 4-5 hours after precipitation, and be washed with water containing ammonium oxalate. The filtrate from the lime determination is slightly acidified and evaporated to about 100cc. About 30 cc. of a saturated solution of ammonia chloride (15°) are then added, the whole neutralised with ammonia, 10 cc. of ammonia (sp.gr. 0·892) being finally added. An excess of about 5 cc. of a saturated solution of Na_2HPO_4 is then added, followed by 40-50 cc. of 10% ammonia. The mixture is allowed to stand in a cool place over night before filtering, and the filtrate is washed with 2·5% ammonia. Nitric acid must not be used in igniting the precipitate of magnesium. S. Kondo.

CHEMISTRY AT INTERFACES.—W. Hardy (*J. Chem. Soc.*, **127**, 1207, 1925).

QUANTITATIVE DETERMINATION OF IRON EXISTING AS FERRO-SILICON IN ARTIFICIAL CORUNDUM.—R. A. Heindl (*J. Amer. Cer. Soc.*, **8**, 671, 1925). The total iron present, whether ferrosilicon or ferric oxide is determined by the combined acid (3 : 1 mixture of conc. HNO_3 and HF) treatment and potassium bisulphate fusion. The ferric oxide is determined by the fusion method with potassium bisulphate, the amount of iron present as ferrosilicon being determined by difference.

VIII.—HISTORICAL, EDUCATIONAL, INSTITUTIONS, ETC.

MASTERPIECES OF GERMAN FAIENCE.—(*Ker. Rund.*, **33**, 359, 1925). An account of an exhibition at Frankfort of XVI–XVIII. Century Middle and South German faience.

THE COLOURED BRICKWORK OF BABYLON.—C. Preusser (*Tonind. Ztg.*, **49**, 972, 1925). Two types of ornamentation were in use at the time of Nebucadnezar, viz.: wallpaintings in coloured enamels and decorated reliefs. Eleven illustrations are given.

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